

SHORT-RANGE CORRELATION IN MOLECULAR PHYSICS:
THE BASIS SET PROBLEM AND THE CORRELATION HOLE

By

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To my wonderful and supportive family and friends, without whom I would never have finished this work.

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The greatest limitation of computational chemistry is the need to solve the Schrödinger equation in a basis set. Because the cost of correlated electronic structure calculations grows rapidly with the size of the basis set while the accuracy does not, predictive correlated calculations are at present feasible only in small molecules. The rapid growth of cost with the number of basis functions is essentially inevitable, but the slow growth of accuracy is not. Rather, this slow growth of accuracy is due to the expansion of the many-electron wavefunction in products of one-electron functions. Because there is a cusp in the wavefunction at the coalescence of electrons which is not properly described in any finite one-particle basis set, this expansion is slowly convergent.

Since the need for large basis sets is caused chiefly by the improper description of the wavefunction for small interelectronic separations, a clever treatment of this regime should obviate the need for large basis sets. By doing so, it would be possible to perform rather accurate correlated calculations for much larger systems than can be studied at present.

Density Functional Theory avoids these difficulties because the object of interest is the electronic density, which is a one-electron function and thus readily described in a single-particle basis set. Since the correlation energy is taken from an analytic model, moreover, so long as the model used properly describes the electronic cusp, Density Functional Theory can provide a route towards treating short-range correlation in a manner which is both accurate and basis set insensitive. Fortunately, the underlying approximation of most current functionals is the local density approximation, in which short-range correlation is treated very accurately.

Therefore, in this work we propose a technique which makes use of the accurate local density approximation for the short-range correlation but which uses the reliable basis set expansion for the remainder. The proposed model, as we will show in what follows, is both conceptually and computationally straightforward, and points the way to ameliorating the need for large basis sets in attaining accurate correlated results.

CHAPTER 1

A NOTATIONAL PROLOGUE

Quantum chemistry is a field plagued with a plethora of acronyms and notational inconsistencies. We have made every effort to be consistent in our notation throughout this work, and introduce it here for reference.

Molecular orbitals are written as φ_p . We will follow the convention that indices a, b, c, \dots correspond to virtual orbitals, while indices i, j, k, \dots correspond to occupied orbitals and indices p, q, r, \dots correspond to arbitrary orbitals. Basis functions are written as χ_μ . The molecular orbitals are expanded in terms of these basis functions as

$$|\varphi_p\rangle = \sum_{\mu} c_p^{\mu} |\chi_{\mu}\rangle. \quad (1.1)$$

These molecular orbitals are all spinorbitals, having coordinates \mathbf{x} , which consist of a spatial part \mathbf{r} and a spin part ξ (that is, a space-spin coordinate is given in bold roman, and a purely spatial coordinate is given in bold italics). Integration over \mathbf{x} is to be understood as integration over \mathbf{r} and summation over ξ . We also often wish to discuss a function of many space-spin variables at a time, or integration over same. Thus, we define

$$\mathbf{X}_{i,k} = \mathbf{x}_i, \mathbf{x}_{i+1}, \dots, \mathbf{x}_k \quad (1.2)$$

where it is to be understood that a function of $\mathbf{X}_{i,k}$ is a function of \mathbf{x}_i through \mathbf{x}_k and integration with respect to $\mathbf{X}_{i,k}$ is equivalent to integration with respect to \mathbf{x}_i through \mathbf{x}_k .

Note that it is common in the literature to write a bra or ket with index p as simply $|p\rangle$, and to write a function of \mathbf{x}_1 as a function just of 1. We have eschewed

these conventions here, but the reader should be aware of their prevalence in the literature.

If we evaluate a property via perturbation theory, we wish to speak of both the contribution from a given order, denoted generically $P^{(k)}$ for the k^{th} -order contribution to the quantity P , and the contribution through a given order, denoted by $P_{[k]}$. That is, we have the partial sum

$$P_{[k]} = \sum_{i=0}^k P^{(i)}. \quad (1.3)$$

The wavefunction is given in general by $|\Psi\rangle$, while the reference determinant (or, in the language of second quantization, the Fermi vacuum) is given by

$$|\Phi\rangle = |0\rangle = |\Psi^{(0)}\rangle. \quad (1.4)$$

The true vacuum is $|\Omega\rangle$, to distinguish it from the Fermi vacuum. Excited determinants are

$$|\Phi_{ab\dots}^{ij\dots}\rangle = |\overset{ij\dots}{ab\dots}\rangle. \quad (1.5)$$

The HF determinant in particular is $|\Phi_{HF}\rangle$, while the KS determinant is $|\Phi_{KS}\rangle$.

The Hamiltonian of interest is generically

$$H = \sum_i h(i) + \frac{1}{2} \sum_{i \neq j} V(r_{ij}), \quad (1.6)$$

where $h(i)$ is the one-electron part, consisting of the kinetic energy $t(i)$ and the potential $v(i) = v_{ext}(i)$. The distance r_{ij} appears frequently in this work; it indicates the norm of the vector $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. Often, we will see the distance between two electrons given by u , which in the foregoing language would be r_{12} . However, the directions of \mathbf{u} and of \mathbf{r}_{12} are opposite: $\mathbf{u} = -\mathbf{r}_{12}$.

We employ a summation convention through this work, with repeated indices to be summed. There are times when it is necessary to sum over only certain indices, however. For this purpose, we indicate all sums explicitly in the equations

in which only certain indices are to be included in the summation. In other words, repeated indices are to be summed in all cases except when summations are explicitly given, in which case *only* those indices for which summation is explicitly indicated are to be summed. Also, there are times when a free index appears multiple times in the same term; sums are not taken over such free indices. We have indicated all such occurrences.

In order to make use of the summation convention, we need a convention for integrals. In accordance with our convention for the second-quantized field operators, we will need to distinguish upper indices from lower indices. One manifestation of this is that if we have $c_p|\Omega\rangle = |\varphi_p\rangle$, we must correspondingly have $\langle\Omega|c^p = \langle\varphi^p|$. Thus, our integral convention must be

$$\langle\varphi^p|O|\varphi_q\rangle = O_q^p \quad (1.7)$$

and

$$\langle\varphi^p\varphi^q|V|\varphi_r\varphi_s\rangle = V_{rs}^{pq}. \quad (1.8)$$

As the convention makes explicit, Hermite conjugation raises a lowered index and lowers a raised index. We thus have

$$(O_q^p)^* = O_p^q. \quad (1.9)$$

Most often, the two electron operator V will be the Coulomb repulsion operator. Because this appears so often, it is given the special symbol

$$\langle\varphi^p\varphi^q|u^{-1}|\varphi_r\varphi_s\rangle = g_{rs}^{pq}. \quad (1.10)$$

Fermi statistics tell us that we will often be interested not in the simple two electron integrals as given above but in their antisymmetrized versions, which are indicated by

$$V_{rs}^{pq} - V_{sr}^{pq} = V_{[rs]}^{pq} = V_{rs}^{[pq]}, \quad (1.11)$$

these two notations being equivalent. In fact, we will wish to antisymmetrize on indices belonging to two different quantities, so we will go so far as to define

$$f_p^{[q} g_r^{s]} = f_p^q g_r^s - f_p^s g_r^q. \quad (1.12)$$

We use Hartree atomic units, in which $e^2 = m_e = \hbar = 1$, throughout this work.

Finally, we use acronyms for the various computational techniques; for reference, these are included here. Those we will need are:

- Hartree-Fock theory (HF)
- Many-Body Perturbation Theory (MBPT)
- Coupled-Cluster Theory (CC), especially with Single and Double excitations (CCSD)
- Density Functional Theory (DFT)
- Kohn-Sham (KS, sometimes KS-DFT)

CHAPTER 2

INTRODUCTION

2.1 The Basis Function Bottleneck

In 1965 [1] Lakin showed that in the expansion of a many-particle atomic wavefunction in one-particle functions with angular momentum ℓ , the contribution to the correlation energy from each level of angular momentum goes as $(\ell + \frac{1}{2})^{-4}$, just as was shown by Schwartz in 1962 [2, 3] for the second-order correlation energy. Thus, many functions of high angular momentum are needed for a proper description of the wavefunction. While the detailed analytic results might differ for molecules, the overall conclusion is the same. This fact complicates things greatly, as the number of basis functions grows rapidly with increasing angular momentum (as $2\ell+1$ if spherical functions are used, or as $\ell(\ell+1)/2$ if Cartesian functions are used), and saturation of a given level of angular momentum is also fairly slow, typically requiring at least six, and often more, contracted Gaussian functions for each type of atomic orbital *i.e.*, to describe angular momentum properly one requires at least six contracted Gaussian functions for each p orbital, and thus eighteen functions in total). It is the basis set size that sets the practical limit on the size of systems that can be treated with various *ab initio* techniques, and while some work has been done on adding back in what is missed in the basis set expansion [4, 5], doing so is difficult at best.

Furthermore, it is unfortunately the case that the correlation energy is much more sensitive to basis set incompleteness than is the single-determinant reference energy because the correlation energy depends explicitly on a two-particle operator rather than on one-particle effective potentials. Thus, while a relatively small basis set is adequate for Hartree-Fock (both in that saturation of a given

angular momentum level is faster and in that higher angular momentum levels are unnecessary), a much larger one is needed for correlated calculations, which are of course essential if one is to have any hope of approaching chemical accuracy. This can be seen easily even with the helium atom by examining the results from several standard basis sets, given in Table 2–1. In this table, and throughout the text, N_{bf} is used to indicate the number of basis functions. For two electron problems, coupled-cluster (CC) [6, 7] with single and double excitations (CCSD) [8] is exact, and hence the only source of error is the incomplete basis set.

Table 2–1: Energy of the He atom in several basis sets, in $-mE_H$

Basis Set	N_{bf}	E_{HF}	E_{CCSD}	ΔE_{corr}
cc-PVDZ	5	2855.16	2887.60	32.44
cc-PVTZ	14	2861.15	2900.35	39.20
cc-PVQZ	30	2861.51	2902.52	41.01
cc-PV5Z	55	2861.62	2903.25	41.63

Clearly, to converge the Hartree-Fock energy to within one mE_H does not require an exceptionally large basis set, and indeed, the triple zeta results are already converged to that accuracy. In contrast, even at the quintuple zeta level, there still appears to be some remaining error in the correlated energy, an illustration of how much more slowly the correlation energy converges with basis set than does the reference energy.

Unfortunately, while it seems fairly obvious that a large basis set is needed for high accuracy, the cost of the usual computational techniques increases rapidly with basis set size. The simplest methods, involving only single determinants and including Hartree-Fock and Kohn-Sham Density Functional Theory [9] scale formally as N_{bf}^4 . More demanding methods such as CCSD scale as N_{bf}^6 or worse. In situations far from equilibrium, in the breaking of double bonds, or in regions of near degeneracy, even CCSD is not enough to provide high accuracy, and more rigorous methods that include higher excitations, such as coupled-cluster with

single, double, triple, and quadruple excitations (CCSDTQ), which scales as N_{bf}^{10} , might be needed [10]. Thus, highly accurate correlated techniques rapidly become unfeasible, both because the basis set cannot be extended far enough to achieve the requisite level of completeness within a given level of correlation and because the level of correlation is limited. For example, suppose we are interested in Si_2O_6 , still not a large molecule with only 76 electrons. Using the versions of the foregoing correlation consistent basis sets for Si and O, we have a very rapid proliferation of basis functions, as shown in Table 2–2, which makes highly accurate computations on even this relatively simple system unfeasible.

Table 2–2: Basis functions for Si_2O_6

Basis Set	$N_{bf,O}$	$N_{bf,Si}$	N_{bf}
cc-PVDZ	14	18	120
cc-PVTZ	30	34	248
cc-PVQZ	55	59	448
cc-PV5Z	91	95	736

At the CCSD level (which we hope will be enough correlation and is for most purposes), the quintuple zeta basis (which we saw we needed for He for high accuracy) has more than six times as many functions as the double zeta, and using the scaling properties of CCSD (that it increases as the number of virtual orbitals to the fourth power), we find that the quintuple zeta calculation requires more than three orders of magnitude more effort than the double zeta; clearly, this scaling becomes prohibitive very quickly. And in cases where we need to do a more accurate treatment of correlation and higher excitations become important, the scaling becomes even worse.

The situation is, of course, helped somewhat by the fact that quantities of chemical interest are almost universally energy differences, which one expects should be less sensitive to basis set incompleteness error than the absolute energies. Further, it can be shown that any Coulomb problem can be formally solved

by methods that scale linearly with system size [11], and this result has been demonstrated already in quantum chemistry by linear scaling in Hartree-Fock [12–14], Density Functional Theory [15], and even CCSD [16, 17]. Unfortunately, we do not wish to rely on cancellation of error, which can be unsystematic, so the fact that the basis set incompleteness error tends to be small for relative energetics is not particularly useful. And linear scaling techniques are only useful for much larger molecules, so performance for smaller systems such as Si₂O₆ shows little improvement.

Thus, it does not seem to be overstating the case to say that the slow convergence with basis set is the greatest unsolved problem in quantum chemistry today. In most cases, the computational chemist must resort to basis set extrapolations of various forms, but while these are certainly useful aids, they have many limitations; they cannot be done for many quantities of interest aside from total energies, analytical gradients are not generally available, and in any case, they require several calculations in increasingly large basis sets to start the extrapolation procedure. It is our hope to help alleviate this basis set problem, which has been attributed to the improper description of the wavefunction near the coalescence of two electrons.

2.2 The Electronic Cusp Condition

That the wavefunction must have a cusp when two charged particles are near each other can be most easily seen by examining

$$\frac{1}{\Psi} H\Psi = \frac{1}{\Psi} T\Psi + V = E. \quad (2.1)$$

As the potential V approaches infinity, the local kinetic energy $\Psi^{-1}T\Psi$ must also approach infinity in such a manner that the two terms add to give a finite total energy. This implies that either the wavefunction vanishes at the coalescence of two charged particles or that the wavefunction has a discontinuous derivative (i.e. a cusp) at the positions where the potential becomes infinite.

The detailed analysis of this cusp fell to Kato [18], who in 1957 showed that the wavefunction at the coalescence of two identical particles with unit charge interacting through a Coulombic potential obeys

$$\frac{d\Psi}{du} \Big|_{u=0} = \frac{1}{2} \Psi|_{u=0} \quad (2.2)$$

where u is the distance between the two particles, assuming they have zero relative angular momentum. The Taylor series is therefore

$$\Psi(u) = \Psi(u=0) \left[1 + \frac{1}{2}u + \dots \right]. \quad (2.3)$$

This result was generalized by Pack and Byers-Brown in 1966 [19] and further generalized by Kutzelnigg and Morgan in 1992 [5] to

$$\Psi = u^k \left(1 + \frac{1}{2(k+1)}u + \dots \right) \quad (2.4)$$

where k controls the symmetries of the wavefunction under exchange and inversion. This so-called "cusp condition" is a feature of any Coulombic system and is thus always present in any quantum chemical calculation, assuming that the only term in the potential which is not analytic at $u = 0$ is the Coulombic interaction between the two electrons (as is almost always the case). An analogous situation exists at the coalescence of electrons and nuclei.

Unfortunately, the standard methodology of quantum chemistry invariably writes the wavefunction in terms of linear combinations of Slater determinants, where each Slater determinant is an anti-symmetric product of single particle functions. Hence, no traditional *ab initio* wavefunction satisfies the electronic cusp condition. Instead, they obey

$$\frac{d\Psi}{du} \Big|_{u=0} = 0 \quad (2.5)$$

irrespective of the relative spins of the two electrons. Thus, the shape of traditional wavefunctions in quantum chemistry is wrong near the coalescence of two electrons.

Given the central importance of the electronic cusp in this work, we will derive (2.2) before discussing the implications of (2.2) and (2.5) for quantum chemistry.

2.2.1 Derivation of the Cusp Condition

Consider a typical molecular electronic Hamiltonian, with electrons interacting with each other via the Coulomb interaction and moving in a fixed potential given by the nuclear framework. Such a Hamiltonian is given by

$$H = -\frac{1}{2} \sum_{i=e^-} \nabla_i^2 - \sum_{A=nuc} \sum_{i=e^-} \frac{Z_A}{r_{iA}} + \frac{1}{2} \sum_{\substack{i,j=e^- \\ i \neq j}} \frac{1}{r_{ij}} + E_{nuc} \quad (2.6)$$

Let us separate out the terms that contain the coordinates of electrons one and two, leaving all terms that do not as H_{other} . The total Hamiltonian is then $H = H_{12} + H_{other}$, with H_{12} given by

$$H_{12} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \sum_{\substack{A=nuc \\ i=1,2}} \frac{Z_A}{r_{iA}} + \sum_{\substack{j=3 \\ i=1,2}}^{N_e} \frac{1}{r_{ij}} + \frac{1}{u}. \quad (2.7)$$

We now change variables to the relative and center-of-mass coordinates

$$\left. \begin{array}{l} \mathbf{u} = \mathbf{r}_2 - \mathbf{r}_1 \\ \mathbf{R} = \frac{1}{2} (\mathbf{r}_1 + \mathbf{r}_2) \end{array} \right\} \iff \left. \begin{array}{l} \mathbf{r}_1 = \mathbf{R} - \frac{1}{2} \mathbf{u} \\ \mathbf{r}_2 = \mathbf{R} + \frac{1}{2} \mathbf{u} \end{array} \right\} \quad (2.8)$$

Expressing H_{12} in terms of these coordinates gives us

$$H_{12} = -\nabla_u^2 - \frac{1}{4} \nabla_R^2 - \sum_{\pm} \frac{Z_A}{\|\mathbf{R}_A - \mathbf{R} \pm \frac{1}{2} \mathbf{u}\|} + \sum_{\pm}^{N_e} \frac{1}{\|\mathbf{R} \pm \frac{1}{2} \mathbf{u} - \mathbf{r}_j\|} + \frac{1}{u}. \quad (2.9)$$

If we expand the terms that couple \mathbf{u} and \mathbf{R} in a Taylor series in \mathbf{u} , we find that the first power of u that appears (aside from the trivial constant) is u^2 ; the linear term cancels out because of the symmetry between the plus and minus

terms.¹ Thus, for small u , the Hamiltonian describing the distance between electrons one and two, $H_{\mathbf{u}}$, is given approximately by

$$H_{\mathbf{u}} = -\nabla_{\mathbf{u}}^2 + \frac{1}{u} + \mathcal{O}(u^2), \quad (2.10)$$

where we have absorbed the constant term into the energy.

The angular part is separable as usual, giving us spherical harmonics and leaving us with a purely radial Hamiltonian H_u of the form

$$H_u = -\frac{1}{u} \frac{d^2}{du^2} u + \frac{\ell(\ell+1)}{u^2} + \frac{1}{u} + \mathcal{O}(u^2). \quad (2.11)$$

Writing the part of the wavefunction in the radial coordinate u as $\Psi(u) = uR(u)$, we have

$$H_u R(u) = -\frac{d^2}{du^2} R(u) + \left(\frac{\ell(\ell+1)}{u^2} + \frac{1}{u} \right) R(u) + \mathcal{O}(u^2) R(u) = E_u R(u). \quad (2.12)$$

For small u , normalizability requires that the wavefunction go as

$$R(u) = u^{\ell+1} + cu^{\ell+2} + \dots \quad (2.13)$$

If we insert this into the short-range radial Schrödinger equation above, we find

$$[-\ell(\ell+1) + \ell(\ell+1)] u^{\ell-1} + [1 - 2c(\ell+1)] u^\ell + \mathcal{O}(u^{\ell+1}) = 0. \quad (2.14)$$

The only detail that interests us here is solving for the constant c , which we obtain by demanding that the coefficient of u^ℓ vanishes. Solving trivially, we have

$$c = \frac{1}{2(\ell+1)}. \quad (2.15)$$

¹ This is true independent of the precise form of the terms which couple \mathbf{u} and \mathbf{R} , assuming only that a Taylor series expansion in \mathbf{u} exists.

Then the wavefunction is given by

$$\Psi(u) = u^l \left[1 + \frac{1}{2(l+1)} u + \dots \right], \quad (2.16)$$

as desired.

2.2.2 Implications of the Cusp Condition

One might hope that failure to obey the cusp condition is not a tremendous problem. After all, since *ab initio* wavefunctions almost invariably are expressed within a basis set of Gaussian functions, the cusp condition at the nucleus is never satisfied, yet by including enough Gaussians with high exponents, reasonable predictions of properties such as NMR coupling constants (which include a term proportional to the spin density at the nuclei) can be made [20]. While it is true, however, that satisfying the cusp condition exactly does not appear to be necessary for good accuracy,² it is found that the shape of the wavefunction near the correlation cusp is poor enough that the description is not even qualitatively good until high angular momentum functions are added. It is the difficulty of describing the region near $u = 0$, not at the point $u = 0$ alone, which causes the slow convergence of correlated techniques with respect to basis set size.

Given these considerations, one might expect that by including a more proper description of the wavefunction near electron coalescence, it would be possible to greatly reduce the size of basis set needed to describe a given system, thus extending the range of applicability of various correlated methods such as Many-Body Perturbation Theory (MBPT), coupled-cluster, and so forth. Further, in systems that can already be treated well within a given level of approximation,

² The cusp condition when written in the usual differential form tells us only about the wavefunction at the point $u = 0$ and as such is not energetically important.

such work might make it possible to describe more accurately systems that can already be treated well within a given level of approximation. There is a long history of such attempts, which merits some attention here; we will discuss only the more prominent.

2.3 Approaches to Treating Short-range Correlation

2.3.1 The Hylleraas Function

The earliest work of this sort may be said to be that of Hylleraas [21], who proposed a functional form for the helium atom ground state wavefunction which included terms with explicit dependence on the distance between the two electrons. Specifically, the Hylleraas function takes the form

$$\Psi = e^{-\zeta(r_1+r_2)} \left[1 + c_1(r_1 + r_2) + c_2(r_1 + r_2)^2 + c_3(r_1 - r_2)^2 + c_4u + c_5u^2 \right], \quad (2.17)$$

where ζ and the coefficients c_i are all to be determined variationally. The optimum parameters yield a total energy of only $0.4 mE_H$ above the estimated nonrelativistic limit for the helium atom. This function does, of course, have a cusp at the coalescence of the two electrons, again demonstrating the importance of properly describing the wavefunction in this region. Note that strict enforcement of the electronic and nuclear cusp conditions for helium worsens the energy by $2 mE_H$, but the accuracy is still remarkable for a wavefunction which has only four parameters (two of the parameters in this case being of course used to enforce the two cusp conditions).

While Hylleraas' approach has the advantages of providing excellent accuracy and being conceptually simple, it has the drawback that the variational optimization is nontrivial. One might hope to avoid optimization of the exponent by choosing a variationally optimum exponent from some other wavefunction such as, for example, choosing the exponent that gives the best Hartree-Fock energy for a minimal basis set of exponential functions (what are known as Slater functions in

quantum chemical circles). Unfortunately, the optimum Hylleraas exponent and the optimum HF exponent give energies that differ by $21 mE_H$ and it is thus clear that choosing an exponent from some other source greatly reduces the accuracy.

A second and more severe drawback of Hylleraas' approach of including interelectronic coordinates in the wavefunction is that difficult integrals are required, especially in molecular calculations. Hence, this approach has been used mainly for benchmark calculations on systems with two to four electrons [22–27], and extending it to treat systems of chemical interest does not seem feasible in the foreseeable future.

2.3.2 Gaussian Geminals

Since explicit inclusion of the interparticle distance in the wavefunction works very well, it has been suggested that basis functions which depend on the interparticle distance could be used in more or less standard correlated theories. This is realized typically by using Gaussian geminal functions as the basis functions of the calculation, as first proposed by Boys [28] and Singer [29]. In the Gaussian geminal approach, the basis functions are taken to be two-particle functions of the form

$$g_{lmn,pqr}(\alpha, \beta, \gamma, \mathbf{A}, \mathbf{r}_1, \mathbf{B}, \mathbf{r}_2) = \chi_{lmn}(\alpha, \mathbf{A}, \mathbf{r}_1) \chi_{pqr}(\beta, \mathbf{B}, \mathbf{r}_2) e^{-\gamma u^2}, \quad (2.18)$$

where

$$\chi_{lmn}(\alpha, \mathbf{R}, \mathbf{r}) = (X - x)^l (Y - y)^m (Z - z)^n e^{-\alpha(\mathbf{r} - \mathbf{R})^2}. \quad (2.19)$$

That is, the two-particle functions are products of the usual basis functions and an extra Gaussian correlation function. Clearly, these fail to satisfy the cusp condition, since these functions are quadratic in the interparticle distance. On the other hand, the description is superior to that given by more standard sets of basis functions, as evidenced by the numerical results. Traditional applications of these basis functions involve non-linear optimization of the correlation exponents, while Persson and

Taylor [30] advocate using a set of fixed values for the correlation exponent and using several geminal functions instead of just one; this vastly simplifies the calculation, at the price of requiring many more integrals. We will consider both options in turn.

Szalewicz *et al.* carried out the optimization of the correlation exponents, and performed MBPT(2), MBPT(3), and CCD calculations on a series of small atoms and molecules [31–35]. In Table 2–3, we report their MBPT results (labeled as as GG) and compare to MBPT using a conventional Gaussian basis set (GTO).

Table 2–3: Energies for some small systems with both GG and conventional GTO, in $-mE_H$

		He	Be	H ₂	LiH
E_{SCF}	GTO	2861.63	14752.99	1133.61	7987.28
	GG	2861.68	14573.02	1133.63	7987.32
$E^{(2)}$	GTO	36.55	58.73	33.74	61.75
	GG	37.37	76.35	34.20	72.18
$E^{(3)}$	GTO	4.09	10.82	4.78	9.00
	GG	3.62	8.87	4.38	6.89
$E_{[3]}$	GTO	40.64	69.55	38.52	70.75
	GG	40.99	85.22	38.58	79.07
$E^{(2)}/E_{corr}$	GTO	86.9%	62.2%	82.6%	74.2%
	GG	88.9%	81.0%	83.7%	86.8%
$E_{[3]}/E_{corr}$	GTO	96.7%	73.8%	94.3%	85.0%
	GG	97.5%	90.4%	94.4%	95.0%

Adapted from K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, *J. Chem. Phys.* **78**, 1420 (1983), Tables II–V (pp. 1425 - 1426), and from K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, *J. Chem. Phys.* **79**, 5543 (1983), Tables I–III, (pp. 5547 - 5548).

The SCF energy of Szalewicz *et al.* is within 10 μE_H of the SCF limit, illustrating the near completeness of their basis, and while the SCF energy with the GTO basis set used here is not as good, the error is still less than 60 μE_H , so that this basis, too, must essentially span the relevant space. At second order, the GG results are noticeably superior to the GTO results, especially for the four-electron systems, despite the expectation that for systems so small, the basis

set error should not be particularly large. At third order, it seems as if the GTO results are essentially the same as the GG results for the two-electron systems, but still markedly inferior for Be and LiH; in fact, for the latter two systems, the GG-MBPT(2) results are better than the GTO-MBPT(3) results, despite the fact that the MBPT(3) is making corrections in the appropriate direction for both methods (which is not always the case). These results suggest that as larger and larger systems are treated, the superiority of the Gaussian geminals should become more and more significant.

In Persson and Taylor's work, a set of six Gaussian correlation functions are chosen (that is, the Gaussian geminals used are products of two standard Gaussian basis functions and a u -dependent Gaussian with exponent γ , and there are six different values of γ used in the same calculation). They examine the neon atom and the water molecule, using standard GTO basis sets augmented with their set of six correlation Gaussians; these results are presented in Table 2-4.

Table 2-4: Second-order valence shell correlation energies, in $-mE_H$

System	Basis	Pair Energy	% Limit
Ne	cc-PVDZ	185.5	57.9
	cc-PVDZ uncontracted	215.5	67.3
	cc-PVDZ uncontracted + 6 GG	290.0	90.6
	cc-PVTZ	264.3	82.5
	cc-PVTZ uncontracted	273.1	85.3
	cc-PVTZ uncontracted + 6 GG	314.0	98.1
H_2O	MBPT(2) Limit	320.2	100
	cc-PVDZ uncontracted	219.8	73.1
	cc-PVDZ uncontracted + 6 GG	277.0	92.2
	MBPT(2) Limit	300.5	100

Adapted from B. J. Persson and P. R. Taylor, *J. Chem. Phys.* **105**, 5915 (1996), Tables VII and VIII (pp. 5923 - 5924).

Obviously, Persson and Taylor's scheme is dramatically superior to using a standard basis set without correlating Gaussians. There is thus some hope that with a relatively standard basis set augmented with a few correlating Gaussians,

one can recover 95% or more of the correlation energy at the MBPT(2) level, even without nonlinear optimization of the type traditionally used in work with Gaussian geminals. It should be recognized, however, that when uncontracted, the cc-PVNZ basis sets contain several more functions than they do when contracted. For example, for neon, cc-PVTZ contains 30 functions, but when uncontracted, this grows to 42, and this increase in the number of basis functions would result in a growth in the computational effort by approximately a factor of four. Unfortunately, Persson and Taylor were not able to run computations with a contracted basis set and additional Gaussian geminal functions, so we can only speculate on how significant the effects of using a contracted basis set would be. Most likely, if the basis set is large enough, the difference between using a contracted GTO basis set and an uncontracted GTO basis set will be modest, but it may become much more significant if smaller basis sets are used. Nonetheless, Persson and Taylor's scheme shows promise as a way of recovering a substantial portion of the correlation energy with a more modest basis set.

As has been seen, using Gaussian geminals as basis functions has the advantage of providing much better accuracy than one can achieve with conventional methods. Further, because the functions are all Gaussian, the integrals are not very difficult. However, there are some problems with this approach as well.

First, traditional correlation techniques such as MBPT(2) need to be formulated for the use of these two particle basis functions, and hence the correlation problem is nontrivial. More troubling, however, is that many body integrals are needed. Even at second order, three-electron integrals are required, and it is only by clever formulation that four-electron integrals can be avoided at this level. Thus, the methods do not scale well with the number of basis functions and the calculations rapidly become expensive. Hence, while the use of Gaussian geminals allows one to do correlated calculations to very high accuracy on systems where a

Hylleraas type wavefunction is unfeasible, it is far from clear that this technique can extend the range of applicability of *ab initio* quantum chemistry.

2.3.3 Explicit R12 Methods

A third type of method including the interelectronic distance in the wavefunction are the so-called explicit R12 methods [36–42]. In these approaches, the electron pair-correlation function is taken to include a term linear in the interparticle distance. For example, to second order, the pair-correlation function for occupied molecular orbitals is taken to be

$$w_{ij}(1, 2) = \sum_{a < b} \varphi_a(1)\varphi_b(2)c_{ij}^{ab} + c_{ij}u\hat{Q}\varphi_i(1)\varphi_j(2), \quad (2.20)$$

where \hat{Q} is a projector onto the occupied space and the first term is the conventional result. When this is substituted into the Hylleraas functional for the second-order energy and minimized, many difficult integrals are found to be needed. In order to evaluate these integrals, completeness insertions are used, and various systematic approximations are then made to account for the finite basis sets that are used in practice. In the so called standard approximation, the integrals ultimately required are

$$\begin{aligned} &\langle \varphi^p \varphi^q | u^{-1} | \varphi_r \varphi_s \rangle \\ &\langle \varphi^p \varphi^q | u | \varphi_r \varphi_s \rangle \\ &\langle \varphi^p \varphi^q | u^2 | \varphi_r \varphi_s \rangle \\ &\langle \varphi^p \varphi^q | \hat{u} \cdot \nabla_u | \varphi_r \varphi_s \rangle \end{aligned} \quad (2.21)$$

Explicit R12 methods (also known as explicitly correlated methods) are, to date, the most routinely applicable correlated methods which go beyond traditional *ab initio* theory. For MP2-R12, the error in the correlation energy decreases by a factor of roughly ten, while the computational effort increases by a factor of roughly five. Note also that five times as many two-electron integrals are needed as in conventional wavefunction theory.

In the limit of a complete basis set, explicit R12 methods satisfy the cusp condition, and even in a finite basis set, the description of the wavefunction near electron coalescence is dramatically better than in traditional methods. This is born out by the convergence properties with angular momentum used in the basis set; MP2-R12 in the standard approximation has truncation error that goes as $(\ell_{max} + 1)^{-7}$, as opposed to as $(\ell_{max} + 1)^{-3}$, as in standard expansions.

This dramatic improvement in convergence can be seen by examining the contributions from each angular momentum (the so-called partial wave increments) in some test cases such as the helium atom. These are shown in Table 2–5 for basis sets of Slater functions and Gaussian functions both.

Table 2–5: Partial-wave increments to $E^{(2)}$ for the He ground state, in $-mE_H$

ℓ	MBPT(2) STO	MBPT(2) GTO	MP2-R12 STO	MP2-R12 GTO
0	13.496	13.495	32.504	32.503
1	18.974	18.973	4.598	4.597
2	3.186	3.129	0.238	0.240
3	0.927	0.864	0.020	0.017
4	0.355		0.002	
Σ^a	36.938	36.461	37.362	37.357

Adapted from V. Termath, W. Klopper, and W. Kutzelnigg, J. Chem. Phys. **94**, 2002 (1991), Table I (p. 2005).

^a Gaussian geminals give an estimated limit of 37.372 mE_H

There are a few things worth noting about these results. First and foremost, the explicitly correlated treatment converges far more rapidly than does the standard MBPT(2) method, as expected, and in fact, it has been checked that the individual partial wave increments do indeed go as $(\ell + \frac{1}{2})^{-8}$, as they should. Secondly, even with only angular momentum up to 3 (*f*-type functions), the explicitly correlated methods give results that agree with the extrapolated total to within a few tens of μE_H , whether Slater or Gaussian type orbitals are used, although Slater orbitals are clearly superior in the conventional MBPT(2) calculations.

Further support for the greatly improved accuracy of these explicitly correlated methods comes from examining the results for several atoms. As can be seen in Table 2–6, the superiority of Slater orbitals over Gaussian orbitals is much reduced in MP2-R12, though this is not the main point of the work. Far more significant, obviously, is the greatly enhanced accuracy of MP2-R12 over standard second-order theory, recovering at least 97% of the second-order energy, and typically much more than that, despite a basis set which yields only 90% or even less of the second-order correlation energy in the usual approach.

Table 2–6: Second-order energies for several atoms, in $-mE_H$

Atom	MBPT(2) STO	MBPT(2) GTO	MBPT(2) Extrap.	MP(2)-R12 STO	MP2-R12 GTO
He	36.938	36.461	37.359	37.362	37.357
Be	75.200	72.995	76.248	76.311	76.036
Mg	414.07	386.6	426.7	426.1	424.3
Ar	685.4	604.8	706.0	706.2	688.8
Ca	767.1	674.9	798.3	797.5	791.0

Adapted from V. Termath, W. Klopper, and W. Kutzelnigg, J. Chem. Phys. **94**, 2002 (1991), from Tables I, II, VI, VIII, and IX (pp. 2005 - 2006, 2011 - 2013).

Finally, in Table 2–7, we examine the performance of the explicitly correlated MP2-R12 method for a series of ten electron systems, all at their experimental equilibrium geometries. The basis set is large enough that the error in the Hartree-Fock energy is minor, although for those systems with multiple hydrogens, this error grows somewhat. The error in conventional MBPT(2) is roughly $40 mE_H$ for these systems; MP2-R12 reduces that error to about $10 mE_H$. Clearly, chemical accuracy at the milliHartree level is not possible in this basis set (though of course the error due to the incomplete treatment of correlation is likely to be much greater than this), but the accuracy is greatly improved nevertheless. Explicitly correlated methods show great promise for increasing the reliability of *ab initio* computation.

Table 2–7: Ground state energy contributions for some ten electron systems, in $-mE_H$

	Ne	HF	H ₂ O	NH ₃	CH ₄
SCF	128 546.96	100 070.22	76 064.75	56 222.85	40 215.68
SCF limit	128 547.01	100 070.82	76 067.5	56 226.	40 219.
MBPT(2)	350.75	339.75	309.65	280.00	237.90
MP2-R12	384.14	370.38	350.32	313.07	265.33
MBPT(2) limit	382.44	378.8	360.47	324.75	274.25

Adapted from W. Kutzelnigg and W. Klopper, J. Chem. Phys. **94**, 2020 (1991), Table II (p. 2022).

All of this, however, assumes that a large enough basis set is used. For the completeness insertion to be approximately justified, at least one function of angular momentum $\ell = 3L_{max}$, where L_{max} is the maximum angular momentum occupied in the reference determinant, must be used (this is because some of the integrals arising from the completeness insertion have partial wave expansions that truncate at L_{max}). Hence, in order to describe water, the basis set should properly include at least one function of *f*-type and must include *d* functions to get results that are at all meaningful. Further, the basis set needs to be nearly saturated through the highest angular momentum used. Also of concern is that the gradients are not trivial and that extra work must be done to ensure that the methods have the appropriate invariance properties to unitary transformations. While explicitly correlated methods show great promise, then, there are still some areas of concern.

2.3.4 Transcorrelated Hamiltonians

Besides attempts to modify the wavefunctions to describe the cusp better, there are various methods which modify the Hamiltonian, making the cusp easier to describe and therefore hopefully alleviating basis set difficulties. Examples of such methods include the transformation originally proposed by Hirschfelder [43], the transcorrelated approach of Boys and Handy [44, 45], the various transformations examined by Nooijen and Bartlett [46], and the Frozen Gaussian Geminal

transformation of Ten-no [47–49]. Here, we will consider only one class of transformations of the Hamiltonian, although there are certainly other possibilities.

The basic approach is to write the wavefunction as

$$|\Psi\rangle = e^G |\Psi_0\rangle, \quad (2.22)$$

where G is a two-particle correlation operator and $|\Psi_0\rangle$ is some reference wavefunction. Then insertion of this expression into the Schrödinger equation gives us

$$e^{-G} H e^G |\Psi_0\rangle \equiv \tilde{H} |\Psi_0\rangle = E |\Psi_0\rangle. \quad (2.23)$$

The transformed Hamiltonian \tilde{H} can be found by using a commutator expansion, which truncates after three commutators because the Hamiltonian contains no more than two-particle operators.

Typically, however, G is taken to consist only of multiplicative operators:

$$G = \frac{1}{2} \sum_{i \neq j} g_{ij} (\mathbf{r}_{ij}). \quad (2.24)$$

In this case, the only non-zero commutators involve the kinetic energy operator and the truncation occurs after two commutators rather than three. When this is the case, the two-particle potential is modified and includes a scalar two-particle potential, a vector two-particle potential, and a three-body potential. More precisely, the transformed Hamiltonian is

$$\tilde{H} = H + K + L \quad (2.25a)$$

$$K = -\frac{1}{4} \sum_{i \neq j} (\nabla_i^2 + \nabla_j^2) g(\mathbf{r}_{ij}) - \sum_{i \neq j} (\nabla_i g(\mathbf{r}_{ij})) \cdot \nabla_{ij} \quad (2.25b)$$

$$L = -\frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}} \nabla_k g(\mathbf{r}_{ik}) \cdot \nabla_k g(\mathbf{r}_{jk}) \quad (2.25c)$$

Because a similarity transformation is used, the left- and right-hand eigenvectors are no longer the same, so calculations of properties require calculation

of the left-hand eigenvector as well as the right-hand eigenvector. It is generally found that with a suitable choice of the correlation operator, the right-hand eigenvector is simpler than in the original Hamiltonian (and hence requires less work to compute), but the left-hand eigenvector is more complicated. This is because the description of the cusp is shifted from being shared by the left- and right-hand eigenvectors equally to being predominantly in only one eigenvector or the other. However, the energy itself requires only the right-hand eigenvector. The situation is entirely analogous to coupled cluster theory, where only the right-hand eigenvector of the similarity transformed Hamiltonian is needed for the energy, but properties require solving the equations for Λ , the left-hand eigenvector [50].

To assess the quality of this method, we consider the work of Ten-no [47]. In pilot calculations, he considered the beryllium atom and the methane molecule. In order to aid the convergence of the calculations (because of concerns about core relaxation effects), he first performed an orbital rotation before calculating the correlation energy to second order. It is this orbital rotation which causes the zeroth- and first-order contributions to the correlation energy. Looking first at the beryllium atom in Table 2–8, one notes that the total correlation energy does exhibit some sensitivity to the basis set, but not a great deal, and that the results are comparable to the results from MP2-R12, though actually a bit lower. For reference, the MBPT(2) limit for the correlation energy is $-76.248 \text{ } mE_H$ [37].

Table 2–8: Beryllium atom correlation energy through second order, in $-mE_H$

Energy Level	$10s6p1d$	$14s9p4d3f$
$E^{(0)}$	57.063	57.046
$E^{(1)}$	1.671	1.680
$E^{(2)}$	19.964	22.001
$E_{[2]}$	78.698	80.727

Adapted from S. Ten-no, Chem. Phys. Lett. **330**, 169 (2000), Table 2 (p. 172).

For methane, the situation is similar; the total energy is somewhat sensitive to basis set, albeit not extremely so, and the results are of a quality comparable to explicit R12 results and with the basis set limit result, which is $-273.579 \text{ } mE_H$ [38]. However, there are some indications that the basis set used is not yet adequate, as can be seen by examining the various partial contributions to the correlation energy, given in Table 2–9. Aside from a small contribution from orbital rotation, $E_V^{(2)}$ corresponds to the conventional second-order energy; the other terms are the second-order contributions from L and K . Note that the direct comparison is between the energies through second order, since in the transcorrelated approach there are first-order contributions to the correlation energy due to the modified operators.

Table 2–9: Methane correlation energy in second order, in $-mE_H$

Term	$10s5p1d$	$11s6p2d1f$
$E_L^{(2)}$	-14.512	-17.508
$E_V^{(2)}$	217.791	243.000
$E_K^{(2)}$	-93.450	-113.800
$E^{(2)}$	109.829	111.692
$E_{[2]}$	278.141	286.309

Adapted from S. Ten-no, Chem. Phys. Lett. **330**, 169 (2000), Table 3 (p. 173).

Obviously, while the total energy is not too different between the two basis sets, the calculation is not yet converged with basis set size, and the basis set is fairly large at this point. The reason for this is that a completeness insertion is used to evaluate some of the integrals, and as is the case with the explicit R12 methods, this will evidently necessitate using a basis large enough that the error caused in the evaluation of the integrals is insignificant.

Handy did much of the original work with the transcorrelated technique [51, 52], and he also considered the beryllium atom. His correlation function took a different form than does Ten-no's and has two parameters. Further, rather than

starting from Hartree-Fock and treating a modified *ab initio* correlation correction only, Handy instead used several coupled equations to evaluate a transcorrelated eigenvalue from the beginning. With a Hartree-Fock energy of $-14.5730 E_H$ in the basis set used, and defining the correlation energy as the difference between the transcorrelated and the Hartree-Fock energies, Handy obtained correlation energies of between $75.2 mE_H$ and $85.9 mE_H$, roughly comparable to both Ten-no's and the explicit R12 results.

The numerical results suggest that this class of methods can give good accuracy in the energy at the cost of introducing extra terms into the Hamiltonian which may be difficult to interpret and, more importantly, difficult to calculate. In particular, integrals involving the new two-body potentials may be non-trivial, and integrals involving the three-body potential are typically both difficult and numerous. Also, while the situation for calculation of the energies is promising, since calculating properties requires solving for the left eigenvector, it is not clear how straightforward and accurate this will be. Handy originally proposed proceeding through the simple Hellmann-Feynman formula, arguing that the wavefunctions should be of high enough quality that the error in making this approximation would be small, but he found that in order to achieve convergence of the expectation values with the quality of the calculation, he had to achieve much greater convergence on the energy than is routine, so this does not seem likely to be of much practical use.

2.3.5 Approximate Potential Methods

Less formal but more physically motivated ideas can also be considered. For example, one can simply replace the Coulombic interactions with various sorts of screened Coulomb potentials (see Figure 2-1); such methods include (but are certainly not limited to) the work of Teter [53], Panas and Snis' regularized SCF procedure [54, 55], the Coulomb attenuated Schrödinger equation of Adamson *et*

al. [56], and the soft Coulomb hole approach of Chakravorty and Clementi [57, 58]. These methods have the advantage of being fairly straightforward to implement and require little new theory. Further, if the Coulomb potential is screened properly, the correlation cusp can be largely removed from the problem, and the wavefunctions for these Hamiltonians are hence smoother and more easily described by a one-particle basis set. It is hoped that any errors caused by using the modified potential would be unimportant. That is, one hopes that the wavefunction will be approximately correct so that properties will be treated reasonably well, and that while the total energy might perhaps be in error, the energy differences will be about correct, since energy differences are what is important in chemistry. But while some results have been reasonably encouraging, such approaches have tended to be rather unsatisfying because they are simply postulated in an *ad hoc* manner, with little or no room for systematic improvement. Further, there is no agreement as to which approximations to make. This is strongly illustrated by the methods named above.

Teter suggests treating electrons as approximately Gaussian charge distributions, so that the electron-electron repulsion is given by

$$V(u) = \frac{\operatorname{erf}\left(\frac{u}{R}\right)}{u}. \quad (2.26)$$

As u becomes small, this potential approaches a constant value, and hence is cuspless. Thus, one would expect it to be easier to describe in a product basis set. In Table 2–10, numerical results are presented for the hydrogen atom, where comparison with the exact energies can be made; here the potential being replaced is not the interaction energy between two electrons but that between the electron and the proton.

Obviously, as the electron density near the nucleus decreases, the agreement with the exact hydrogen eigenvalues gets vastly superior. Since in a correlated

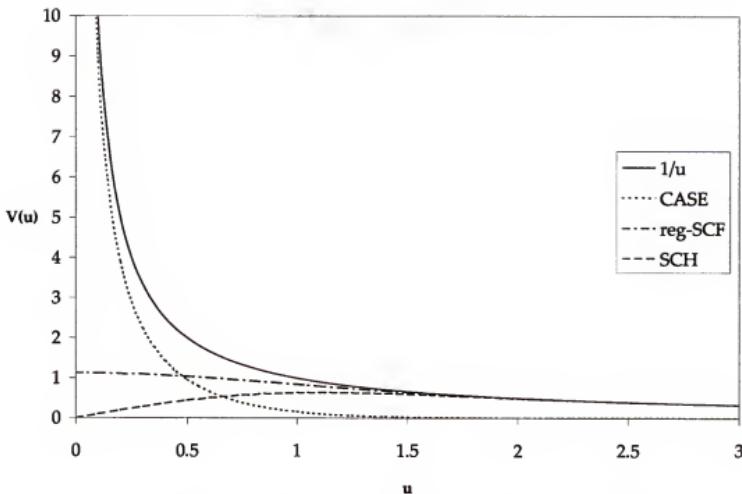


Figure 2–1: Various effective potentials, all with parameter $R = 1$

calculation, the potential of interest is repulsive rather than attractive, one would expect that it might be possible to get reasonable energies with parameters that are not unduly small. Unfortunately, the accurate description of the wavefunction requires larger parameters, so that the potential is less singular. Thus, there is some tension between the need for accuracy in the eigenvalues and the need for accuracy of the basis set expansion. Whether this tension can be easily resolved or not is unclear.

Panas and Snis arrive at the same potential from different considerations. Their argument is that writing the wavefunction as products of single particle functions is a constraint which makes the description of the cusp improper. Since the Hartree-Fock description of the wavefunction is chemically appealing and gives an excellent qualitative agreement in most cases, the natural thing to do would be to remove the cusp from the problem. To this end, they truncate an integral

Table 2–10: Hydrogen atom energies in $-mE_H$, using the potential of (2.26)

State	$R = 1$	$R = 0.5$	$R = 0.25$	$R = 0.125$	$R = 0.0625$	exact
1s	331.14	412.96	464.68	488.30	496.61	500.00
2s	101.45	113.52	120.49	123.53	124.58	125.00
2p	122.79	124.74	124.98	125.00	125.00	125.00
3s	48.28	52.08	54.21	55.12	55.43	55.56
3p	54.81	55.47	55.55	55.56	55.56	55.56
3d	55.55	55.56	55.56	55.56	55.56	55.56

Data from M. Teter, private communication.

representation of the Coulomb potential,

$$\frac{1}{u} = \frac{2}{\sqrt{\pi}} \int_0^{\infty} ds e^{-s^2 u^2} \longrightarrow \frac{2}{\sqrt{\pi}} \int_0^{\frac{R}{u}} ds e^{-s^2 u^2} = \frac{\text{erf}\left(\frac{u}{R}\right)}{u}, \quad (2.27)$$

where the parameter R depends on the basis functions involved. Further, they propose a correction to the kinetic energy due to the absence of the cusp, which involves an approximation to the complementary error function which they have removed from the potential. Results for the total energies of several small atoms are given in Table 2–11, using a $7s7p$ atomic natural orbital basis set.

Table 2–11: Total atomic energies, in $-mE_H$

Atom	ROHF	reg-ROHF	exact
He	2 861.6	2 884.4	2 903.7
Li	7 432.7	7 470.6	7 478.1
Be	14 573.0	14 637.7	14 667.4
B	24 529.1	24 622.0	24 653.9
C	37 688.6	37 815.1	37 845.0
N	54 400.8	54 566.4	54 589.3
O	74 811	75 044	75 067
F	99 410	99 722	99 734
Ne	128 547	128 951	128 939

Adapted from I. Panas and A. Snis, Theor. Chem. Acc. **97**, 232 (1997), Table 2 (p. 236).

One can see that the regularized ROHF method gives lower, presumably superior total energies to standard Hartree-Fock in all cases, although there is still

some noticeable residual error. One possible area of concern is illustrated clearly by the results for the neon atom, however: because the Hamiltonian is modified, the energy may be below the exact result, and the reg-RHF procedure calls for minimization of the total energy. While in general the lack of a variational bound on the energy is not of great concern so long as the method is known to be close to the exact solution, solving a modified problem variationally is worrisome, and more experimentation is needed.

In contrast to the suggestions of Teter, Panas, and Snis, in their Coulomb attenuated Schrödinger equation method, Adamson *et al.* advocate using instead

$$V(u) = \frac{1 - \operatorname{erf}\left(\frac{u}{R}\right)}{u}, \quad (2.28)$$

essentially because the rest of the potential is approximately a smooth background, so that neglecting it has minor effects on the wavefunction and energy differences despite disastrous total energies. (We should note that this proposal is not intended to make describing the wavefunction easier, but we mention it to illustrate the amount of disagreement as to what parts of the Coulomb potential are important.). This potential tends to the regular Coulomb potential as u becomes small, but goes to zero much faster for large u .

To get some sense of the effect of this potential on the wavefunction, Adamson *et al.* examined the ground state of the hydrogen atom, evaluating the correction to the energy and the wavefunction through first order in perturbation theory; results are presented in Table 2-12.

The quantity in the second column is the exact eigenvalue for the CASE, while $E_{CASE}^{(0)} + E_{CASE}^{(1)}$ is the first-order result, perturbing around the regular hydrogen atom. The coefficient $c_{2s}^{(1)}$ is the first order coefficient of the $2s$ wavefunction in the perturbed $1s$ wavefunction. As R becomes large, the energy becomes fairly reasonable, and the wavefunction changes relatively little from the unperturbed

Table 2-12: Hydrogen atom ground state in the CASE model

R	E_{CASE}	$E_{CASE}^{(0)} + E_{CASE}^{(1)}$	$c_{2s}^{(1)}$
10	-0.388270	-0.388266	0.0003
100	-0.488717	-0.488717	3×10^{-6}
1000	-0.499887	-0.499887	3×10^{-9}
∞	-0.500000	-0.500000	0

Adapted from R. D. Adamson, J. P. Dombroski, and P. M. W. Gill, Chem. Phys. Lett. **254**, 329 (1996), Table 1 (p. 331).

1s function. Thus, Adamson and coworkers propose the idea that while neglecting what they call the background (that is, the contribution of $\text{erf}(\frac{u}{R})/u$) is a gross error insofar as determining energies, it makes relatively little difference to the wavefunction. Their hope is that the error in the energy will be systematic, so that energy differences will essentially exhibit cancellation of error.

The potential energy curve for H₂ should partially answer the question of whether the energy differences will indeed be approximately correct or not, and the answer seems to be in the affirmative, as none of the spectroscopic parameters is changed significantly and the curves are essentially superimposable (as seen in Figure 2-2).

Thus, it seems that the error made in neglecting the background may well not be significant in examining processes that conserve the number of electrons. It must be noted, however, that these results are obtained at the Hartree-Fock level only. The authors make some attempt to examine correlation energies by evaluating the second-order energy using the orbital eigenvalues from the full potential and comparing to the exact second-order energy. The changes are slight, but this is not a consistent calculation, since the authors point out that the occupied orbital energies change dramatically and the virtual orbital energies are approximately constant. A true correlated calculation might be of interest, to see if the background contributes much at the correlated level. Again, we stress that

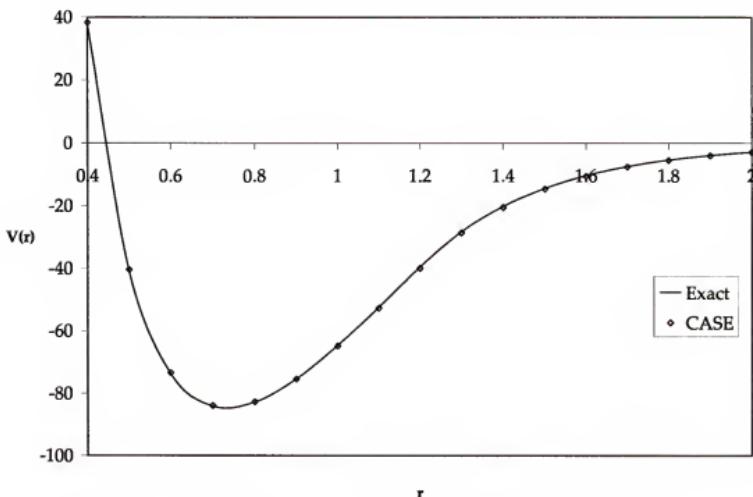


Figure 2-2: UHF H₂ potential energy curve, in kcal/mol vs. Å

Adapted from R. D. Adamson, J. P. Dombroski, and P. M. W. Gill, Chem. Phys. Lett. **254**, 329 (1996), Table 3 (p 333).

while this method would not improve the situation with regards to basis set, it does illustrate the dramatic differences in opinion as to which modified potentials might be of interest.

One last approach is the soft Coulomb hole method of Chakravorty and Clementi. They propose using a potential of the form

$$V(u) = \frac{1 - e^{-(\frac{u}{R})^2}}{u}, \quad (2.29)$$

where the constant R depends on the basis functions involved and is parameterized with four parameters for each type of angular momentum. When using these screened Coulomb integrals in a Hartree-Fock calculation, one retains much of the basis set insensitivity of normal single determinant methods; because the potential depends on the basis set, of course, the results do illustrate somewhat greater basis-set dependence than do normal Hartree-Fock calculations. However, the results are

much less sensitive than are those from a true correlated calculation, yet the model recovers some of the important effects of electron correlation, at least insofar as total energies are concerned.

This can be seen in Table 2–13, where we examine the ionization potentials calculated for the first row atoms. Obviously, the ionization potentials, at least, are treated much more accurately with the soft Coulomb hole than they are with Hartree-Fock. Thus, this method, too, shows promise for reasonable accuracy.

Table 2–13: First ionization potentials for several atoms, in eV

Atom	Hartree-Fock	Soft Coulomb Hole	Experiment
Li	5.34	5.39	5.39
Be	8.04	9.28	9.32
B	7.93	8.17	8.30
C	10.79	11.07	11.26
N	13.96	14.29	14.53
O	11.89	13.61	13.62
F	15.72	17.44	17.42
Ne	19.85	21.58	21.56

Adapted from S. J. Chakravorty and E. Clementi, Phys. Rev. A **39**, 2290 (1989), Table I (p. 2293).

While it is encouraging that these various approximate potential techniques can be chosen so as to yield decent accuracy with inexpensive calculations, the wide variety in the possibilities which seem to have promise is somewhat disheartening. Further, it is unclear how to systematically improve the results one might get from these methods, since ultimately the exact answer with an approximate potential will be incorrect. For these reasons, one would prefer a less pragmatic and more rigorous derivation of such potentials, so that if they are some approximation to a more rigorous theory, one could see what theory it is they are approximating, and what terms are being excluded.

In fact, since the transcorrelated Hamiltonian approach modifies the usual two-body interaction, these effective potential methods can be seen as approximations

to the rigorous transcorrelated Hamiltonian in which the three-body terms and the gradient portion of the two-body terms have been neglected. The relative success of these effective potential models in turn suggest that the three-body term and the gradient term in the transcorrelated Hamiltonian approach may be treated in some approximate manner without losing a reasonable degree of accuracy.

2.4 Constraints on the Model

Given the number of different suggested approaches, it should prove useful to establish a list of desiderata that any proposed method for dealing with the cusp problem should satisfy. Naturally, this list will not be unique, but we consider the following things to be of most importance.

1. The method must be computationally practical for atoms and molecules.
2. The method should be as mathematically rigorous as possible and should contain few if any parameters.
3. The method should yield high accuracy.
4. The method should be exact for two electrons.
5. The method should satisfy the virial theorem.
6. It should be possible to practically and accurately treat gradients and other properties in addition to the energy.

Notice that we do not demand that the cusp condition itself be satisfied; as mentioned, numerical data shows this to be less important. What we do want is for the dominant effects of the short range part of electron correlation (which is where conventional techniques fail) to be included.

Criterion 1 is met only by the approximate potential method; all others require many-body integrals which are difficult and time-consuming, and most of the other methods face additional difficulties as well. In contrast, criterion 2 is met by all the methods but the approximate potential techniques, although it should be noted that Gaussian geminal and transcorrelated Hamiltonians use completeness insertions to aid in the evaluation of difficult integrals, and these completeness

insertions are in practice approximations. Criterion 3 is also met by all techniques but approximate potential methods. The fourth criterion is of course met by none of these methods except in the complete basis set Full CI limit, which is not useful since standard techniques are also exact for two electrons in this limit. Criterion 5 is violated by approximate potential methods and the transcorrelated Hamiltonian technique, since these modify the potential which gives us the virial theorem in the first place. Finally, the sixth criterion is met by none of the above methods, since only modified potential methods are computational straightforward and it is these methods which fail to give good total energy. While they may indeed give good properties in most cases, this relies on cancellation of error, which is neither systematic nor satisfying.

2.5 The Unifying Theme

It may seem that, aside from the cusp condition, there is little to unify these approaches. This is not, in fact, the case; these methods can be viewed as various attempts to model the two-particle density matrix in a basis set, for it is this quantity which is essential for the description of interacting electrons. It is from this perspective that we shall approach this problem in the remainder of this work. In order to do so, however, we need to make a digression into the two-particle density matrix and the various methods we may use to calculate it.

CHAPTER 3

DENSITY MATRICES AND WAVEFUNCTIONS

When we solve the Schrödinger equation, we generate a complicated wavefunction which depends on the coordinates of every electron in the system. This seems wasteful in some sense, as we are almost never interested in any properties which depend on the coordinates of more than two electrons at a time. If we can find some function which encapsulates all the information about two electrons, then we can evaluate any one- or two-electron property, *i.e.*, essentially any property of interest. The appropriate function turns out to be the two-particle reduced density matrix (often referred to as simply the two-matrix). Because the two-matrix is a particular case of the more general k -particle reduced density matrix, we discuss the latter.

3.1 The k -Particle Reduced Density Matrix

Let us suppose that we have a normalized wavefunction Ψ which depends on the coordinates of N electrons. Then the k -particle reduced density matrix [59–62] can be defined through

$$n_k(\mathbf{X}_{1,k}; \mathbf{X}'_{1,k}) \equiv \binom{N}{k} \int d\mathbf{X}_{k+1,N} \Psi^*(\mathbf{X}_{1,k}, \mathbf{X}_{k+1,N}) \Psi(\mathbf{X}'_{1,k}, \mathbf{X}_{k+1,N}). \quad (3.1)$$

The part in which $\mathbf{x}_i = \mathbf{x}'_i \forall i$ is said to be the diagonal part, sometimes called the k -density. We often refer to the two-density as the pair density.

Several properties of the k -matrix should be pointed out. First, it is manifestly Hermitian. That is, we have

$$n_k(\mathbf{X}_{1,k}; \mathbf{X}'_{1,k}) = n_k^*(\mathbf{X}'_{1,k}; \mathbf{X}_{1,k}). \quad (3.2)$$

Second, the k -matrix determines all density matrices of lower order, through repeated use of the relation

$$n_{k-1}(\mathbf{X}_{1,k-1}; \mathbf{X}'_{1,k-1}) = \frac{k}{N+1-k} \int d\mathbf{x}_k n_k(\mathbf{X}_{1,k-1}, \mathbf{x}_k; \mathbf{X}'_{1,k-1}, \mathbf{x}_k). \quad (3.3)$$

Lastly, the cusp condition (2.4) on the wavefunction manifests itself in the density matrix as well. In particular, for the pair density, the Kato cusp condition (2.2) on the singlet wavefunction becomes the Kimball cusp condition [63] on the two-matrix,

$$\left. \frac{dn_2}{du} \right|_{u=0} = n_2|_{u=0}. \quad (3.4)$$

3.1.1 Basis Set Expansion of the k -Matrix

If we have a complete basis of orthonormal one-particle functions (*e.g.*, a set of molecular orbitals), we can represent the k -matrix simply by

$$n_k(\mathbf{x}_1 \dots \mathbf{x}_k; \mathbf{x}'_1 \dots \mathbf{x}'_k) = \Gamma_{p_1 \dots p_k}^{q_1 \dots q_k} \varphi^{p_1}(\mathbf{x}_1) \dots \varphi^{p_k}(\mathbf{x}_k) \varphi_{q_1}(\mathbf{x}'_1) \dots \varphi_{q_k}(\mathbf{x}'_k). \quad (3.5)$$

The matrix element $\Gamma_{p_1 \dots p_k}^{q_1 \dots q_k}$ is also called the k -matrix, and in some sense may be regarded as a more fundamental quantity. Due to Fermi statistics, Γ must be antisymmetric under the interchange of any two indices (we require, of course, that these indices both be upper or both be lower). The recursion relation (3.3) can be expressed as

$$\Gamma_{p_1 \dots p_{k-1}}^{q_1 \dots q_{k-1}} = \frac{k}{N+1-k} \Gamma_{p_1 \dots p_{k-1} r}^{q_1 \dots q_{k-1} r}. \quad (3.6)$$

Of course, if we can give no prescription for finding Γ , the foregoing is of no use. Such a prescription exists, however, and makes use of the machinery of second quantization, a brief overview of which is presented in Appendix A. As the derivation is not particularly enlightening, we merely state the result,

$$\Gamma_{p_1 \dots p_k}^{q_1 \dots q_k} = \frac{1}{k!} \langle \Psi | c_{p_1} \dots c_{p_k} c^{q_k} \dots c^{q_1} | \Psi \rangle, \quad (3.7)$$

and refer the reader to Appendix B for details. Note the order of indices on the field operators.

3.1.2 Uses of the k -Matrix

Density matrices are useful quantities because they allow us to evaluate expectation values without direct reference to a wavefunction. If we have a symmetric k -particle operator \mathcal{O} (*i.e.*, one which is a summation of operators which act the same way on all combinations of k electrons), then its expectation value is given simply by

$$\begin{aligned}\langle \mathcal{O} \rangle &= \text{tr}(\mathcal{O} n_k) \\ &= \int d\mathbf{X}_{1,k} d\mathbf{X}'_{1,k} \mathcal{O}(\mathbf{X}'_{1,k}; \mathbf{X}_{1,k}) n_k(\mathbf{X}_{1,k}; \mathbf{X}'_{1,k}).\end{aligned}\quad (3.8)$$

Here, we see the utility of the term “density matrix.” The analogue of matrix multiplication is seen to be integration over a common set of coordinates (and just as in matrix multiplication, the coordinates in common should be the second set for the first matrix and the first set for the second matrix), and the analogue of the trace is integration along the diagonal. In the equation above, for example, the integration over $\mathbf{X}_{1,k}$ constitutes the matrix multiplication, and the subsequent integration over $\mathbf{X}'_{1,k}$ is the trace of the resulting product.

Given that we can evaluate any property we desire knowing only the density matrix of the appropriate rank, one may wonder why the wavefunction is necessary at all; the variational principle would suggest that if we were to find the two-matrix which minimizes the energy, we would have the best two-matrix possible, and from this, we could find any other quantity of chemical interest we might desire.

There is, unfortunately, a flaw in this reasoning: namely, we must ensure that the two-matrix we use corresponds to a fermionic wavefunction. This is commonly known as the N-representability problem, and while a solution does exist, it turns out to be no simpler than it is to find a wavefunction and evaluate the two-matrix directly [64].

3.2 Wavefunction Theories

Since, as we have seen, it is not practical to optimize the two-matrix directly, we are forced to construct it through a wavefunction of some sort. Obviously, any attempt to be exhaustive on the topic of wavefunction theories is beyond the scope of this work. However, we will need some details on the wavefunctions actually used here. These all fall under one of three categories: Hartree-Fock (HF), Many-Body Perturbation Theory (MBPT), and Coupled-Cluster (CC). We will discuss each in turn. More detail can be found in the text by Szabo and Ostlund [65].

3.2.1 Hartree-Fock Theory

The simplest model for the wavefunction that we will consider is HF theory. We assume an anti-symmetrized product of orthonormal one-particle functions (in other words, a Slater determinant of molecular orbitals) and optimize the functions so as to yield the lowest total energy, defining the energy to be the expectation value of the Hamiltonian with respect to this determinant. This approximation is tantamount to replacing the actual electron-electron interaction with an averaged electron-electron interaction. Because only these average features are treated, the sensitivity to basis set is much reduced.

If we use the HF wavefunction to find the expectation value of the Hamiltonian, we arrive at the energy expression for a single determinant,

$$E = h_i^i + \frac{1}{2} g_{ij}^{[ij]}. \quad (3.9)$$

With this energy we associate a matrix of Lagrange multipliers λ which enforce the constraint of orthonormal orbitals, giving us a Lagrangian of the form

$$\mathcal{L} = E - \lambda_k^l (\langle \varphi^k | \varphi_l \rangle - \delta_l^k). \quad (3.10)$$

Differentiation with respect to φ^k leads us immediately to

$$F |\varphi_k\rangle = \lambda_k^l |\varphi_l\rangle, \quad (3.11)$$

where F is the Fock operator, defined as

$$F(1) = h(\mathbf{x}_1) + \int d\mathbf{x}_2 \varphi^j(\mathbf{x}_2) \frac{1 - P_{12}}{r_{12}} \varphi_j(\mathbf{x}_2). \quad (3.12)$$

Here, the operator P_{12} interchanges the indices 1 and 2. For future purposes, it proves convenient to define the Coulomb and exchange operators here, as well. The Coulomb operator is

$$J(1) = \int d\mathbf{x}_2 \varphi^j(\mathbf{x}_2) \frac{1}{r_{12}} \varphi_j(\mathbf{x}_2), \quad (3.13)$$

while the (non-local) exchange operator is

$$K(1) = \int d\mathbf{x}_2 \varphi^j(\mathbf{x}_2) \frac{P_{12}}{r_{12}} \varphi_j(\mathbf{x}_2), \quad (3.14)$$

This notation is meant to indicate that F , J , and K act on electron one, and allows us to write the Fock operator in its simplest form as

$$F = h + J - K. \quad (3.15)$$

This operator is manifestly invariant to unitary transformations among the occupied orbitals, and λ is manifestly Hermitian and hence diagonalizable by such a transformation. Thus, we write the HF equations in their canonical form after making this transformation,

$$F |\varphi_k\rangle = \epsilon_k |\varphi_k\rangle. \quad (3.16)$$

In the foregoing equation, there is no summation over k .

Note that there is no mention so far of virtual orbitals. However, the Fock operator has an infinite spectrum of eigenvalues, and its eigenfunctions other than those occupied in our reference determinant form the virtual orbitals. In any finite basis, of course, we get only a finite number of virtual orbitals, which is not important for HF theory because the virtual orbitals have no effect on the energy.

Hartree-Fock theory has several important properties. First, the orbital eigenvalues correspond roughly to ionization potentials and electron affinities,

as proven first by Koopmans. This correspondence is far from close enough for chemical accuracy, but is often qualitatively correct. A second important property is that the HF determinant does not mix with singly excited determinants across the Hamiltonian, so that

$$\langle \Phi_{HF} | H | \Phi_a^i \rangle = 0. \quad (3.17)$$

This result is known as Brillouin's Theorem. One of its implications is that the Hartree-Fock one-matrix is correct through first order in electron correlation, a result known as the Möller-Plesset Theorem. Finally, the HF one-matrix \mathbf{P} is idempotent, a result which holds for any single-determinantal wavefunction.

3.2.2 Many-Body Perturbation Theory

While HF is conceptually simple, it is not accurate enough for most chemical purposes because it lacks a description of electron correlation. We can recover such a description perturbatively, of course, and this is often done with MBPT. Before we can adequately explain MBPT, however, we must first discuss Rayleigh-Schrödinger perturbation theory (RSPT) so as to highlight the differences between MBPT and RSPT. For simplicity, we assume a Hartree-Fock reference throughout. Rayleigh-Schrödinger perturbation theory with the partitioning of the Hamiltonian which is of interest to us is usually known as Möller-Plesset perturbation theory (MP).

In both MP and MBPT, we write the total Hamiltonian as

$$H = H^{(0)} + H^{(1)} \quad (3.18a)$$

$$H^{(0)} = \sum_i F(i) \quad (3.18b)$$

$$H^{(1)} = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} - \sum_i (J(i) - K(i)) \quad (3.18c)$$

and our wavefunction and energy as

$$\Psi = \Psi^{(0)} + \Psi^{(1)} + \dots \quad (3.19)$$

$$E = E^{(0)} + E^{(1)} + \dots \quad (3.20)$$

The zeroth-order wavefunction $\Psi^{(0)}$ is the HF determinant Φ_{HF} , while $E^{(0)}$ is the sum of occupied orbital energies. The other eigenstates of $H^{(0)}$ are the other determinants formed by the HF orbitals; each has an energy given by the sum of orbital energies. Because in general $E_{[1]}$ is the expectation value of the full Hamiltonian with respect to the zeroth-order wavefunction, and this is the energy functional of HF theory, we have trivially that the HF energy is correct through first order. Correlation thus contributes to the energy at second order and higher, though it contributes to the wavefunction at first order.

Regardless of the actual partitioning of the Hamiltonian, the energy can be evaluated in many possible ways. Most trivially, we can project the zeroth-order wavefunction onto the n^{th} -order Schrödinger equation, giving

$$E_{RSPT}^{(n)} = \langle \Psi^{(0)} | H^{(1)} | \Psi^{(n-1)} \rangle. \quad (3.21)$$

Sufficient manipulation eventually allows this to be brought to a form in which only the wavefunctions up to order $k = \lfloor \frac{n}{2} \rfloor$ are necessary. Alternatively, we may use the form

$$E_{RSPT}^{(n)} = \left[\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right]^{(n)}, \quad (3.22)$$

in which we must expand the denominator perturbatively as well as the numerator. Finally, we may write

$$E_{RSPT}^{(n)} = (\langle \Psi | H | \Psi \rangle)^{(n)} \quad (3.23)$$

and impose the additional constraint that the wavefunction is normalized to unity through n^{th} order. All of these forms are completely equivalent. The specific choice

of (3.18b) for $H^{(0)}$ and any of the above formulae for the energy define the n^{th} order MP energy.

Many-body perturbation theory is quite similar, and gives numerically identical results. The difference lies in the treatment of unlinked terms (for a discussion of diagrammatic techniques and terminology, see Appendix A). Due to the linked-diagram theorem, we know that all unlinked terms in the energy sum to zero, so MBPT explicitly drops them from the energy; the n^{th} -order MBPT energy expression is thus

$$E_{MBPT}^{(n)} = (\langle \Psi | H | \Psi \rangle_L)^{(n)}, \quad (3.24)$$

where the subscript “ L ” indicates only linked diagrams contribute. Note that there is no normalization denominator left; this is because the terms which arise from it, known as renormalization terms, are all explicitly unlinked.

In addition to the cancellation of unlinked diagrams in the energy expression, we find that all unlinked diagrams in the wavefunctions also cancel. It is the cancellation of unlinked diagrams which makes MBPT an extensive method, like HF and CC and unlike a truncated Configuration Interaction (CI). Since we will need MBPT wavefunctions later, we present their general form. We find

$$|\Psi^{(n)}\rangle = [(R_0 W)^n |\Psi^{(0)}\rangle]_L, \quad (3.25)$$

where

$$R_0 = \frac{1 - |\Psi^{(0)}\rangle \langle \Psi^{(0)}|}{E^{(0)} - H^{(0)}} \quad (3.26)$$

and

$$W = H^{(1)} - E^{(1)}. \quad (3.27)$$

A more convenient form is as a finite order coupled-cluster expansion, but we will postpone using this representation for the moment.

3.2.3 Coupled-Cluster Theory

While the many-body expansion is powerful, it has several disadvantages. In particular, a perturbative expansion will break down if the perturbation is large, such as in bond breaking processes. Also, the cost grows very rapidly with respect to the order to which the calculation is performed. Thus, it would be desirable to find a form for the wavefunction which retains the extensivity advantages of MBPT while eliminating its disadvantages. Such a form is provided by CC theory, which sums MBPT diagrams to infinite order quickly and conveniently, thus offering superior accuracy. In practice, one must approximate the full CC wavefunction, but even an approximate CC wavefunction contains at least some terms of all orders.

In CC theory, the wavefunction is written as

$$|\Psi\rangle = e^T |0\rangle, \quad (3.28)$$

where T is

$$T = \sum_{n=1}^N T_n \quad (3.29)$$

and T_n creates n -tuply excited determinants out of the reference determinant $|0\rangle$.

That is, it takes the form

$$T_n = \frac{1}{(n!)^2} t_{i_1 i_2 \dots i_n}^{a_1 a_2 \dots a_n} c_{a_1} c^{i_1} c_{a_2} c^{i_2} \dots c_{a_n} c^{i_n}. \quad (3.30)$$

If we insert this ansatz into the Schrödinger equation, we rapidly arrive at

$$e^{-T} H e^T |0\rangle = E |0\rangle. \quad (3.31)$$

Projection from the left by the reference determinant yields the energy, while projection by excited determinants yield the algebraic equations necessary to specify the T_n operators. The similarity transformed Hamiltonian $e^{-T} H e^T$ is

commonly written as \bar{H} , and can also be written, using the Baker-Campbell-Hausdorff commutator expansion, as

$$\bar{H} = (He^T)_C, \quad (3.32)$$

where the subscript “ C ” indicates only connected diagrams are to be included.

3.3 Calculating the Two-Matrix

Having given a brief overview of the wavefunction techniques involved, we turn now to extracting the two-matrix from the above wavefunctions. Using (3.5) with the special case of $k = 2$ gives us

$$n_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \Gamma_{pq}^{rs} \varphi^p(\mathbf{x}_1) \varphi^q(\mathbf{x}_2) \varphi_r(\mathbf{x}'_1) \varphi_s(\mathbf{x}'_2) \quad (3.33)$$

where

$$\Gamma_{pq}^{rs} = \frac{1}{2} \langle \Psi | c_p c_q c^s c^r | \Psi \rangle. \quad (3.34)$$

Different ansätze for the wavefunction correspond to different expressions for Γ_{pq}^{rs} .

Before we calculate the two-matrices from various wavefunctions, however, let us pause briefly to discuss their general structure.

3.3.1 Structure of the Two-Matrix

We can write the string $c_p c_q c^s c^r$ as the normal-ordered part plus all possible contractions, using Wick’s theorem. The effect is that we have three types of terms to consider: terms with no field operators, terms with two field operators, and terms with four field operators. This last term, the pure two-particle term, we will write as $\bar{\Gamma}_{pq}^{rs}$.

Let us write the full one-matrix as γ . There will be a part with no field operators which we will call \mathcal{P} and a part with two field-operators in normal order, which we denote by $\bar{\gamma}$. As a matrix equation, this is

$$\gamma = \mathcal{P} + \bar{\gamma}. \quad (3.35)$$

Note that in direct analogy with the two-matrix, we have for the one-matrix γ

$$\gamma_p^q = \langle \Psi | c_p c^q | \Psi \rangle, \quad (3.36)$$

while for $\bar{\gamma}$, we have instead

$$\bar{\gamma}_p^q = \langle \Psi | \{c_p c^q\} | \Psi \rangle. \quad (3.37)$$

With these conventions, we find, after sufficient algebra,

$$\Gamma_{pq}^{rs} = \frac{1}{2} (\gamma_p^{[r} \gamma_q^{s]} - \bar{\gamma}_p^{[r} \bar{\gamma}_q^{s]}) + \bar{\Gamma}_{pq}^{rs}. \quad (3.38)$$

(Recall that brackets enclosing a pair of indices indicate antisymmetrization.) This result can be shown in the following manner.

Writing the two-matrix as an expectation value, we have

$$\Gamma_{pq}^{rs} = \frac{1}{2} \langle c_p c_q c^s c^r \rangle, \quad (3.39)$$

which, using Wick's theorem, is

$$\begin{aligned} \Gamma_{pq}^{rs} &= \frac{1}{2} \langle \{c_p c_q c^s c^r\} \rangle + \frac{1}{2} (\delta_p^r \langle \{c_q c^s\} \rangle + \delta_p^r \delta_q^s + \delta_q^s \langle \{c_p c^r\} \rangle) \\ &\quad - \frac{1}{2} (\delta_p^s \langle \{c_q c^r\} \rangle + \delta_p^q \delta_q^r + \delta_q^r \langle \{c_p c^s\} \rangle). \end{aligned} \quad (3.40)$$

Factoring and adding and subtracting a term, we have

$$\begin{aligned} \Gamma_{pq}^{rs} &= \frac{1}{2} \langle \{c_p c_q c^s c^r\} \rangle + \frac{1}{2} (\delta_p^r + \langle \{c_p c^r\} \rangle) (\delta_q^s + \langle \{c_q c^s\} \rangle) - \frac{1}{2} \langle \{c_p c^r\} \rangle \langle \{c_q c^s\} \rangle \\ &\quad - \frac{1}{2} (\delta_p^s + \langle \{c_p c^s\} \rangle) (\delta_q^r + \langle \{c_q c^r\} \rangle) + \frac{1}{2} \langle \{c_p c^s\} \rangle \langle \{c_q c^r\} \rangle. \end{aligned} \quad (3.41)$$

Recognizing $\bar{\Gamma}$ and $\bar{\gamma}$, and noting also that the Kronecker delta and its expectation value are the same, we simplify a little to get

$$\Gamma_{pq}^{rs} = \bar{\Gamma}_{pq}^{rs} - \frac{1}{2} \bar{\gamma}_p^r \bar{\gamma}_q^s + \frac{1}{2} \langle \delta_p^r + \{c_p c^r\} \rangle \langle \delta_q^s + \{c_q c^s\} \rangle - \frac{1}{2} \langle \delta_p^s + \{c_p c^s\} \rangle \langle \delta_q^r + \{c_q c^r\} \rangle. \quad (3.42)$$

Using Wick's theorem in reverse on the final expectation values gives us the desired result.

In position space, this factorization of the two-matrix becomes

$$\begin{aligned} n_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) &= \frac{1}{2}n_1(\mathbf{x}_1; \mathbf{x}'_1)n_1(\mathbf{x}_2; \mathbf{x}'_2) - \frac{1}{2}n_1(\mathbf{x}_1; \mathbf{x}'_2)n_1(\mathbf{x}_2; \mathbf{x}'_1) \\ &\quad + n_2^{corr}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2). \end{aligned} \quad (3.43)$$

Some of the terms in the two-matrix above can be given a simple physical interpretation, especially when we consider the diagonal elements only. In this limit, the first term corresponds to the Coulomb term in HF theory, but with the exact density (hence, it is the true classical term in the pair density). Similarly, the second term in the pair density corresponds to the exchange term in HF theory, using the exact one-matrix; this term can hence be regarded as the “true” exchange contribution. The remaining piece accounts for correlation; the matrix elements defining what we have called n_2^{corr} are

$$\Xi_{pq}^{rs} = \bar{\Gamma}_{pq}^{rs} - \frac{1}{2}\bar{\gamma}_{[p}^r\bar{\gamma}_{q]}^s. \quad (3.44)$$

Note that the Kimball cusp condition of (3.4) implies that the pair density has a term linear in u in its series expansion for small u . However, because the Coulomb part and the exchange part are both written as symmetric products of functions of \mathbf{x}_1 and \mathbf{x}_2 , they do not contain any term linear in u . The Kimball cusp condition, in other words, is a phenomenon only of correlation.

Having written the two-matrix in a general form, we now turn to its specific manifestation. We begin with HF theory. Although second quantization techniques are not necessary for Hartree-Fock, they simplify things enormously for correlated wavefunctions, so we will employ them here as well.

3.3.2 The Hartree-Fock Two-matrix

The Hartree-Fock two-matrix is particularly simple. First, note that both $\bar{\Gamma}$ and $\bar{\gamma}$ vanish, since these come from the expectation value of normal-ordered products of field operators, and the expectation value of a normal-ordered product

vanishes when taken with respect to the Fermi vacuum. Thus, we have simply

$$(\Gamma_{pq}^{rs})_{HF} = \frac{1}{2} P_p^{[r} P_q^{s]}, \quad (3.45)$$

where \mathbf{P} is the Hartree-Fock one-matrix. This explicitly illustrates again that HF theory does not contain detailed information about the behavior of two electrons. Thus, in the position space representation we have

$$\begin{aligned} n_2^{HF}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) &= \frac{1}{2} [n_1^{HF}(\mathbf{x}_1; \mathbf{x}'_1) n_1^{HF}(\mathbf{x}_2; \mathbf{x}'_2) \\ &\quad - n_1^{HF}(\mathbf{x}_1; \mathbf{x}'_2) n_1^{HF}(\mathbf{x}_2; \mathbf{x}'_1)]. \end{aligned} \quad (3.46)$$

The foregoing is true, of course, whether the orbitals are Hartree-Fock orbitals or not and is simply a manifestation of the approximation that the wavefunction is a single determinant.

In order to proceed, we need the HF one-matrix, the calculation of which is fortunately trivial. Using (3.36), we have

$$P_p^q = \langle 0 | c_p c^q | 0 \rangle. \quad (3.47)$$

Note that if either of the indices p or q is virtual, the vacuum is annihilated. As is to be expected, then, the only non-vanishing term in the one-matrix is the occupied-occupied term, and it is clear that the HF one-matrix in fact takes the form

$$\mathbf{P} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad (3.48)$$

where the matrix is split into occupied and virtual sectors.

Thus, the Hartree-Fock two-matrix is given by

$$n_2^{HF}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \frac{1}{2} \delta_i^{[k} \delta_j^{l]} \varphi^i(\mathbf{x}_1) \varphi^j(\mathbf{x}_2) \varphi_k(\mathbf{x}'_1) \varphi_l(\mathbf{x}'_2) \quad (3.49)$$

which reduces to

$$\begin{aligned} n_2^{HF}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) &= \frac{1}{2} \varphi^i(\mathbf{x}_1) \varphi^j(\mathbf{x}_2) \varphi_i(\mathbf{x}'_1) \varphi_j(\mathbf{x}'_2) \\ &\quad - \frac{1}{2} \varphi^i(\mathbf{x}_1) \varphi^j(\mathbf{x}_2) \varphi_j(\mathbf{x}'_1) \varphi_i(\mathbf{x}'_2). \end{aligned} \quad (3.50)$$

Note that the Hartree-Fock contribution to the two-matrix is already correctly normalized (this is true, of course, for the Hartree-Fock k -matrix in general). This imposes the constraint that

$$\text{tr}(\Gamma - \Gamma_{HF}) = 0. \quad (3.51)$$

3.3.3 The Perturbative Two-Matrix

In general, an n^{th} order contribution to some expectation value is given by

$$\langle O^{(n)} \rangle = [\text{tr}(\Gamma \mathbf{O})]^{(n)}. \quad (3.52)$$

Thus, for second order, we need the first- and second-order two-matrices, one-matrices, and wavefunctions. Recall, however, that the Möller-Plesset theorem tells us that the first-order correction to the one-matrix vanishes given a HF reference.

It may seem strange that the second-order wavefunction is apparently needed for evaluating an expectation value at second-order, since the energy is an expectation value and requires only the first-order wavefunction. That is, we have for the energy

$$E^{(2)} = \text{tr}(\Gamma^{(1)} \mathbf{H}^{(1)}) + \text{tr}(\Gamma^{(2)} \mathbf{H}^{(0)}), \quad (3.53)$$

but the second term can be written in terms of the first-order density matrix. To see this explicitly, we write the second term in more detail:

$$\begin{aligned} \text{tr}(\Gamma^{(2)} \mathbf{H}^{(0)}) &= \langle \Psi^{(1)} | H^{(0)} | \Psi^{(1)} \rangle \\ &\quad + \langle \Psi^{(2)} | H^{(0)} | \Psi^{(0)} \rangle + \langle \Psi^{(0)} | H^{(0)} | \Psi^{(2)} \rangle. \end{aligned} \quad (3.54)$$

Using the zeroth-order and first-order Schrödinger equations, and collecting terms, we rewrite this as

$$\begin{aligned} \text{tr} (\Gamma^{(2)} \mathbf{H}^{(0)}) &= E^{(0)} (\langle \Psi | \Psi \rangle)^{(2)} + E^{(1)} (\langle \Psi | \Psi \rangle)^{(1)} \\ &\quad - \frac{1}{2} (\langle \Psi^{(1)} | H^{(1)} | \Psi^{(0)} \rangle + \langle \Psi^{(0)} | H^{(1)} | \Psi^{(1)} \rangle). \end{aligned} \quad (3.55)$$

In density matrix language, this is just

$$\text{tr} (\Gamma^{(2)} \mathbf{H}^{(0)}) = E^{(0)} \text{tr} (\Gamma^{(2)}) + \frac{1}{2} E^{(1)} \text{tr} (\Gamma^{(1)}) - \frac{1}{2} \text{tr} (\Gamma^{(1)} \mathbf{H}^{(1)}) \quad (3.56a)$$

$$= -\frac{1}{2} \text{tr} (\Gamma^{(1)} \mathbf{H}^{(1)}), \quad (3.56b)$$

where we have used the trace condition (3.51). We thus have

$$E^{(2)} = \frac{1}{2} \text{tr} (\Gamma^{(1)} \mathbf{H}^{(1)}). \quad (3.57)$$

Hence, the second-order two-matrix is not necessary for evaluating the second-order energy, though it is needed for evaluating any other two-electron property through second-order.

Calculating a density matrix via perturbation theory is complicated somewhat by the normalization requirement, since the expressions we have used for the k -matrix assume a normalized wavefunction, which we do not get from perturbation theory without taking special care. There are two approaches one might take, given this. If one were to write the perturbed wavefunction as

$$|\Psi\rangle = \Omega |\Psi^{(0)}\rangle, \quad (3.58)$$

where Ω is the wave operator, then a property would be given through a perturbative estimate of the expectation value:

$$\langle O \rangle_{[k]} = \left[\frac{\langle \Psi^{(0)} | \Omega^\dagger O \Omega | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Omega^\dagger \Omega | \Psi^{(0)} \rangle} \right]_{[k]}, \quad (3.59)$$

where we recall that the subscript $[k]$ indicates expansion through order k . This can be applied to calculating the two-matrix, where the operator O becomes a string of field operators. Note that using the Hamiltonian as the operator of interest gives us the RSPT energy expression (3.22).

Alternatively, a biorthogonal approach can be taken, in which the right-hand wavefunction is written as

$$|\Psi_R\rangle = \Omega_R |\Psi^{(0)}\rangle \quad (3.60)$$

and the left-hand wavefunction is written as

$$\langle \Psi_L | = \langle \Psi^{(0)} | \Omega_L. \quad (3.61)$$

The wave operators Ω_R and Ω_L are chosen in such a way as to maintain normalization, *i.e.*,

$$\langle \Psi^{(0)} | \Omega_L \Omega_R | \Psi^{(0)} \rangle = 1. \quad (3.62)$$

With this approach, a property would instead be given by

$$\langle O \rangle_{[k]} = [\langle \Psi^{(0)} | \Omega_L O \Omega_R | \Psi^{(0)} \rangle]_{[k]}. \quad (3.63)$$

Again, note the resemblance to the MBPT energy expression (3.24).

The reader may wonder whether these two approaches are equivalent. The answer of course depends on the nature of the wavefunctions. For both CC and MBPT, we can write

$$\Omega_R = e^T \quad (3.64)$$

$$\Omega_L = (1 + \Lambda) e^{-T}. \quad (3.65)$$

With a Hartree-Fock reference, we find

$$T^{(1)} = T_2^{(1)} \quad (3.66)$$

$$T^{(2)} = T_1^{(2)} + T_2^{(2)} + T_3^{(2)} \quad (3.67)$$

$$\Lambda^{(1)} = \left(T_2^{(1)} \right)^\dagger \quad (3.68)$$

$$\Lambda^{(2)} = \left(T_1^{(2)} + T_2^{(2)} + T_3^{(2)} \right)^\dagger. \quad (3.69)$$

If we now evaluate the first-order contribution to an expectation value, (3.59) gives

$$\langle O \rangle^{(1)} = \langle \Psi^{(0)} | (T^{(1)})^\dagger O + OT^{(1)} | \Psi^{(0)} \rangle, \quad (3.70)$$

and (3.63) gives us the same, once we note that $T^{(1)}$ annihilates the vacuum when acting to the left.

The second-order contributions are rather more involved. From the expectation value form (3.59), we have

$$\begin{aligned} \langle O \rangle^{(2)} &= \langle \Psi^{(0)} | (T^{(2)} + \frac{1}{2} T^{(1)} T^{(1)\dagger} O + O(T^{(2)} + \frac{1}{2} T^{(1)} T^{(1)\dagger}) | \Psi^{(0)} \rangle \\ &\quad + \langle \Psi^{(0)} | (T^{(1)})^\dagger O T^{(1)} | \Psi^{(0)} \rangle - \langle \Psi^{(0)} | (T^{(1)})^\dagger T^{(1)} | \Psi^{(0)} \rangle \langle \Psi^{(0)} | O | \Psi^{(0)} \rangle. \end{aligned} \quad (3.71)$$

This can be simplified by noting that $|\Psi^{(0)}\rangle\langle\Psi^{(0)}| = 1 - |\Psi_k^{(0)}\rangle\langle\Psi^{(0),k}|$, where $|\Psi_k^{(0)}\rangle$ is an excited zeroth-order determinant. If we insert this, we will find a contribution that looks like

$$\langle \Psi^{(0)} | (T^{(1)})^\dagger T^{(1)} | \Psi^{(0)} \rangle_k. \quad (3.72)$$

But because $T^{(1)}$ contains only double excitations, this looks like the matrix element between a doubly-excited state and a state of higher than double excitation, and therefore terms of this form vanish. Thus,

$$\langle \Psi^{(0)} | (T^{(1)})^\dagger T^{(1)} | \Psi^{(0)} \rangle \langle \Psi^{(0)} | O | \Psi^{(0)} \rangle = \langle \Psi^{(0)} | (T^{(1)})^\dagger T^{(1)} O | \Psi^{(0)} \rangle. \quad (3.73)$$

Equivalently, we may use

$$\langle \Psi^{(0)} | (T^{(1)})^\dagger T^{(1)} | \Psi^{(0)} \rangle \langle \Psi^{(0)} | O | \Psi^{(0)} \rangle = \langle \Psi^{(0)} | O (T^{(1)})^\dagger T^{(1)} | \Psi^{(0)} \rangle, \quad (3.74)$$

or, finally, the clearly Hermitian form. This leaves us with

$$\begin{aligned} \langle O \rangle^{(2)} &= \langle \Psi^{(0)} | (T^{(2)} + \frac{1}{2} T^{(1)} T^{(1)})^\dagger O + O (T^{(2)} + \frac{1}{2} T^{(1)} T^{(1)}) | \Psi^{(0)} \rangle \\ &\quad + \langle \Psi^{(0)} | (T^{(1)})^\dagger O T^{(1)} - \frac{1}{2} (T^{(1)})^\dagger T^{(1)} O - \frac{1}{2} O (T^{(1)})^\dagger T^{(1)} | \Psi^{(0)} \rangle. \end{aligned} \quad (3.75)$$

In contrast, the biorthogonal form (3.63) gives us at second order

$$\begin{aligned} \langle O \rangle^{(2)} &= \langle \Psi^{(0)} | (T^{(2)})^\dagger O + O (T^{(2)} + \frac{1}{2} T^{(1)} T^{(1)}) | \Psi^{(0)} \rangle \\ &\quad + \langle \Psi^{(0)} | (T^{(1)})^\dagger O T^{(1)} - (T^{(1)})^\dagger T^{(1)} O | \Psi^{(0)} \rangle. \end{aligned} \quad (3.76)$$

These two forms (3.76) and (3.75) differ only by $\langle \Psi^{(0)} | \frac{1}{2} (T^{(1)} T^{(1)})^\dagger O | \Psi^{(0)} \rangle$, which vanishes assuming that the operator acts on no more than three electrons at a time. Thus, the two general forms (3.59) and (3.63) give identical answers through second order for any property except those which depend on four or more electrons at a time. This, incidentally, justifies our use of the expectation value form in showing that the second-order wavefunction is not needed for the second-order energy.

These preliminaries out of the way, we turn to evaluating the MBPT one- and two-matrices. Note that either the expectation value form or the biorthogonal form will give identical results, as we are concerned only with one- and two-body operators here. In fact, because this is so, we need not write the left-hand wavefunctions explicitly, and can use the Hermitian adjoints of the right-hand wavefunctions in their place.

The first-order wavefunction is made only of double excitations; it takes the form

$$|\Psi^{(1)}\rangle = \frac{1}{4} (t_{ij}^{ab})^{(1)} |\Phi_{ab}^{ij}\rangle, \quad (3.77)$$

where

$$(t_{ij}^{ab})^{(1)} = \frac{g_{ij}^{[ab]}}{\epsilon_{ijab}}, \quad (3.78)$$

there is no summation in the above, and in general

$$\epsilon_{i_1 \dots i_k a_1 \dots a_k} = (\epsilon_{i_1} + \dots + \epsilon_{i_k}) - (\epsilon_{a_1} + \dots + \epsilon_{a_k}). \quad (3.79)$$

The second-order wavefunction includes single, double, and triple excitations, as well as a contribution from $(T^{(1)})^2$, *i.e.*, a disconnected quadruple. Thus, the second-order wavefunction is

$$\begin{aligned} |\Psi^{(2)}\rangle &= (t_i^a)^{(2)} |\Phi_a^i\rangle + \frac{1}{4} (t_{ij}^{ab})^{(2)} |\Phi_{ab}^{ij}\rangle + \frac{1}{36} (t_{ijk}^{abc})^{(2)} |\Phi_{abc}^{ijk}\rangle \\ &\quad + \frac{1}{32} (t_{ij}^{ab})^{(1)} (t_{kl}^{cd})^{(1)} |\Phi_{abcd}^{ijkl}\rangle. \end{aligned} \quad (3.80)$$

The details of the coefficients are not particularly relevant.

With these perturbed wavefunctions, the perturbative one-matrix is given through second-order by

$$\gamma_{[2]} = \mathbf{P} + \gamma^{(2)}. \quad (3.81)$$

If we insert our first- and second-order wavefunctions, we find that the second-order one-matrix is

$$\begin{aligned} (\gamma_p^q)^{(2)} &= (t_a^i)^{(2)} \langle \Phi_a^i | c_p c^q | 0 \rangle + (t_i^a)^{(2)} \langle 0 | c_p c^q | \Phi_a^i \rangle \\ &\quad + \frac{1}{16} (t_{ij}^{ab})^{(1)} (t_{cd}^{kl})^{(1)} \langle \Phi_{kl}^{cd} | c_p c^q | \Phi_{ab}^{ij} \rangle. \end{aligned} \quad (3.82)$$

Note that there are no contributions from $T_2^{(2)}$, $T_3^{(2)}$, or $(T_2^{(1)})^2$. This is because a double or higher excitation cannot couple to the ground state across a one-particle operator such as $c_p c^q$. Evaluating these various terms is simple, tedious, and not

very illuminating. Thus, we merely present the results, which are that

$$(\gamma_j^k)^{(2)} = -\frac{1}{2} (t_{ij}^{ab})^{(1)} (t_{ab}^{ik})^{(1)} \quad (3.83a)$$

$$(\gamma_c^b)^{(2)} = \frac{1}{2} (t_{ij}^{ab})^{(1)} (t_{ac}^{ij})^{(1)} \quad (3.83b)$$

$$(\gamma_i^a)^{(2)} = (t_i^a)^{(2)} \quad (3.83c)$$

$$(\gamma_a^i)^{(2)} = (t_a^i)^{(2)}. \quad (3.83d)$$

Note that the trace condition (3.51) is explicitly satisfied by the above form.

In contrast to the one-matrix, the two-matrix has corrections even at first order; as noted, it is only these corrections which are needed for the second-order energy. The first-order corrections to the two-matrix are

$$(\Gamma_{pq}^{rs})^{(1)} = \frac{1}{8} (t_{ab}^{ij})^{(1)} \langle \Phi_{ij}^{ab} | c_p c_q c^s c^r | 0 \rangle + \frac{1}{8} (t_{ij}^{ab})^{(1)} \langle 0 | c_p c_q c^s c^r | \Phi_{ab}^{ij} \rangle. \quad (3.84)$$

These matrix elements are simple to evaluate, but note first that the only non-zero contributions are to $(\Gamma_{kl}^{cd})^{(1)}$ and $(\Gamma_{cd}^{kl})^{(1)}$. If we actually evaluate these matrix elements, we find simply

$$(\Gamma_{kl}^{cd})^{(1)} = \frac{1}{2} (t_{kl}^{cd})^{(1)}. \quad (3.85)$$

We can generate $(\Gamma_{cd}^{kl})^{(1)}$ by using Hermiticity of the two-matrix.

The second-order two-matrix is significantly more complicated, given as it is by

$$(\Gamma_{pq}^{rs})^{(2)} = \langle \Psi^{(0)} | (T^{(2)})^\dagger c_p c_q c^s c^r + c_p c_q c^s c^r T^{(2)} + (T^{(1)})^\dagger [c_p c_q c^s c^r, T^{(1)}] | \Psi^{(0)} \rangle. \quad (3.86)$$

Once again, the actual evaluation of the matrix elements is not of interest. We have

$$\left(\Gamma_{ij}^{kl}\right)^{(2)} = \frac{1}{4} \left(t_{ab}^{kl}\right)^{(1)} \left(t_{ij}^{ab}\right)^{(1)} + \frac{1}{4} \left(t_{ab}^{m[k]}\right)^{(1)} \delta_{[j]}^l \left(t_{i|m}^{ab}\right)^{(1)} \quad (3.87a)$$

$$\left(\Gamma_{ij}^{ka}\right)^{(2)} = \frac{1}{2} \left(t_{[j]}^a\right)^{(2)} \delta_{i]}^k \quad (3.87b)$$

$$\left(\Gamma_{ij}^{ab}\right)^{(2)} = \frac{1}{2} \left(t_{ij}^{ab}\right)^{(2)} \quad (3.87c)$$

$$\left(\Gamma_{ia}^{jb}\right)^{(2)} = \frac{1}{4} \left(t_{ac}^{kl}\right)^{(1)} \left(t_{kl}^{bc}\right)^{(1)} \delta_i^j - \frac{1}{2} \left(t_{ac}^{jk}\right)^{(1)} \left(t_{ik}^{bc}\right)^{(1)} \quad (3.87d)$$

$$\left(\Gamma_{ia}^{bc}\right)^{(2)} = 0 \quad (3.87e)$$

$$\left(\Gamma_{ab}^{cd}\right)^{(2)} = \frac{1}{4} \left(t_{ab}^{ij}\right)^{(1)} \left(t_{ij}^{cd}\right)^{(1)}. \quad (3.87f)$$

The other ten elements may be generated by making use of anti-symmetry on the lower or upper indices and Hermiticity of the entire two-matrix.

With sufficient exertion, the reader may verify the following identities:

$$tr(\Gamma^{(1)}) = 0 \quad (3.88a)$$

$$tr(\Gamma^{(2)}) = 0 \quad (3.88b)$$

$$\left(\Gamma_{pr}^{qr}\right)^{(1)} = \frac{N-1}{2} (\gamma_p^q)^{(1)} = 0 \quad (3.88c)$$

$$\left(\Gamma_{pr}^{qr}\right)^{(2)} = \frac{N-1}{2} (\gamma_p^q)^{(2)}. \quad (3.88d)$$

3.3.4 The Coupled-Cluster Two-Matrix

Like the MBPT two-matrix, the CC two-matrix could be calculated both through an expectation value form and through a biorthogonal form. Unlike in MBPT, however, the expectation value form is dramatically more complicated, and in fact cannot be given in a simple closed form. Thus, we choose to work with the biorthogonal form here as well. We will consider only the CCSD two-matrix; others may be of interest, but CCSD is already complicated enough.

Recall that in CCSD, the T operator is truncated after double excitations. This means that the operator Λ should contain only single and double excitations

as well. We have, then,

$$\Lambda = \Lambda_1 + \Lambda_2 \quad (3.89)$$

$$T = T_1 + T_2 \quad (3.90)$$

where

$$\Lambda_1 = \lambda_a^i c_i c^a \quad (3.91)$$

$$\Lambda_2 = \frac{1}{4} \lambda_{ab}^{ij} c_i c^a c_j c^b \quad (3.92)$$

$$T_1 = t_i^a c_a c^i \quad (3.93)$$

$$T_2 = \frac{1}{4} t_{ij}^{ab} c_a c^i c_b c^j \quad (3.94)$$

We cannot give closed form expressions for the various t and λ amplitudes, so we will leave the two-matrix defined in terms of these various parameters.

If we write out the two-matrix, we have

$$(\Gamma_{pq}^{rs})^{CCSD} = \frac{1}{2} \langle 0 | (1 + \Lambda) (c_p c_q c^s c^r e^T)_C | 0 \rangle. \quad (3.95)$$

The result is by no means enlightening, and here we merely note that now the two-particle density matrix contains all of the following (here, “o” indicates an occupied part and “v” indicates a virtual part): Γ_{oo}^{oo} , Γ_{vv}^{vv} , Γ_{ov}^{ov} , Γ_{vo}^{vv} , Γ_{oo}^{ov} , and Γ_{vv}^{vo} , as well as the appropriate conjugates (of course, no summation over o or v is taken in the above). Details are given in Appendix B.

3.4 The Two-Matrix and Intracules

Thus far, we have presented the two-matrix as an abstraction, a useful quantity which aids in computation, but have not discussed its interpretation. Indeed, the physical interpretation of the full two-matrix is somewhat obscure, as it depends on four coordinates for two electrons. The diagonal part $n_2(\mathbf{x}_1, \mathbf{x}_2)$, however, tells us the probability that if electron one has coordinates \mathbf{x}_1 then electron two has coordinates \mathbf{x}_2 , aside from normalization issues; more precisely,

with the normalization we have chosen, the two-density tells us the number of electron pairs in which one has coordinates \mathbf{x}_1 and the other has coordinates \mathbf{x}_2 .

A related quantity is the position intracule, defined through an integration as

$$P(u) = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \delta(r_{12} - u) n_2(\mathbf{x}_1, \mathbf{x}_2). \quad (3.96)$$

In other words, setting aside the issue of spin for the moment, the position intracule tells us the number of electron pairs separated by a distance u . It can be decomposed into various spin components, so that we have intracules for a pair of electrons both with up spin, for a pair of electrons both with down spin, and for a pair of electrons with opposite spin.

We need not restrict ourselves to this one-dimensional quantity, and can of course consider more general distributions like

$$P(\mathbf{u}) = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \delta(\mathbf{r}_{12} - \mathbf{u}) n_2(\mathbf{x}_1, \mathbf{x}_2). \quad (3.97)$$

These intracules are important because the most important two-electron operator for chemical applications is the electron repulsion operator, whether that is taken to have the usual Coulomb form or is modified in one of the effective potential methods discussed in Chapter 2. This operator depends only on the distance between electrons, and therefore, for purposes of evaluating the electron interaction energy, even the diagonal part of the two-matrix contains far more information than we need. If we knew the position intracule for some system, we could evaluate the electronic interaction energy trivially via

$$E_{ee} \equiv \langle V_{12} \rangle = \int_0^\infty du P(u) V_{12}(u). \quad (3.98)$$

While the position intracule, then, does not contain sufficient information to evaluate more general two-particle properties (such as the expectation

value of S^2 , for instance), it contains everything we need for evaluating the electron repulsion energy. We shall return to this quantity in our discussion of the exchange-correlation hole, but before we can do so, we must present the Kohn-Sham construction in Density Functional Theory.

CHAPTER 4

DENSITY FUNCTIONAL THEORY AND THE TWO-MATRIX

Density Functional Theory is an appealing alternative to wavefunction theory for many reasons, the most obvious being that the electronic density is a much simpler quantity with which to work. In particular, because the electronic density depends only on the coordinates of one electron, it is relatively insensitive to the basis set, and one might hope to use this insensitivity to alleviate the problems associated with correlated wavefunctions. It is not immediately clear, however, how one can connect the two, and it is this connection which we will develop in this chapter. Along the way, we will discuss several features of DFT and the electron gas. The literature on the field is vast; for references see Parr and Yang's text [9] and references contained therein.

4.1 Foundations of Density Functional Theory

The theoretical underpinnings of DFT are the Hohenberg-Kohn (HK) theorems [66], which tell us that the electronic density is sufficient to determine all properties of interest, although they do not tell us how this is to be done. To be more precise, the theorems tell us that the density determines the potential and that for a given Hamiltonian, if one wishes to find the exact density, one may search over all densities and find the one which yields the lowest energy. The upshot of these statements, however, is that the density is the only variable needed to determine the energy or anything else of interest. That the density uniquely determines everything may seem a little surprising. There is, however, an argument which lends it credence, due originally to E. Bright Wilson.

The density determines the number of electrons by simple quadrature. Thus, all terms in the Hamiltonian but the external potential are determined trivially. In

the case of a molecular Hamiltonian, one could examine the density for cusps; their location determines the location of the nuclei, and their exact form determines the charge of the nuclei (this follows from the analogue of the nuclear cusp condition for densities). Knowing the locations and charges of all the nuclei, we can write the external potential, and thus the total Hamiltonian. Therefore, the density is sufficient to specify the Hamiltonian. Once the Hamiltonian is specified, any property of interest can be calculated, so clearly the density is sufficient to determine everything about the system.

It is implicitly assumed that the density corresponds to a wavefunction which is the ground-state of a Hamiltonian of the usual form, *i.e.*, one which contains a multiplicative external potential. Such a density is known as *v-representable*. Second, the Hamiltonian is limited to non-degenerate ground-states. Last, we cannot determine the form of the electron-electron interaction potential. Rather, we must assume a form.

The first two objections are removed by the constrained search formalism. Here, we define the energy from the density in the following manner:

$$E[n] = v_{ext}[n] + \min_{\Psi \rightarrow n} \langle \Psi | T + V_{ee} | \Psi \rangle. \quad (4.1)$$

This eliminates the restriction to non-degenerate Hamiltonians because we choose that ground-state wavefunction from among the degenerate set which yields the density of interest. It eliminates the v-representability condition for a more subtle reason, which is that by introducing wavefunctions in the minimization step, we have guaranteed that the densities over which we minimize are v-representable.

The last objection is not overcome here, nor is it particularly relevant. For any given choice of the electronic interaction potential, the HK theorems hold; it is only when there are multiple possible choices of the electronic interaction potential that they do not.

More important by far than any of these other considerations is that while the HK theorems tell us that in principle it is possible to determine anything we care to determine about a system solely through the density, they do not tell us how we are to accomplish this. We will briefly review some implementations of the scheme next.

4.2 Implementations of Density Functional Theory

If we write the total electronic energy for a system, only a few terms can be given explicitly in terms of the density, namely the external potential and the Coulomb contribution to the electronic interaction energy. Exchange, correlation, and kinetic energy all require more detailed knowledge of the system, and any DFT method must approximate these quantities in some way.

The simplest approximation to the expectation value of some operator \mathcal{O} is the local density approximation (LDA). In this approximation, one writes the expectation value of the operator as

$$\langle \mathcal{O} \rangle = \int d\mathbf{r} n(\mathbf{r}) o[n(\mathbf{r})]. \quad (4.2)$$

Here, the quantity $o[n(\mathbf{r})]$ is the density of whatever property we are interested in and is taken to be a functional of only the density at the point in space at which we evaluate it. This is then taken from some model, usually the homogeneous electron gas (HEG).

Thus, for example, the exchange energy would be calculated in the following manner within the LDA. Suppose that the density of the system of interest at the point \mathbf{r} is $n(\mathbf{r}) = \rho$. For an HEG of density ρ , the exchange energy density is $\epsilon_x(\rho) = -C_x \rho^{\frac{1}{3}}$, as we shall show later. Then the exchange energy contained in the volume $d\mathbf{r}$ about the point \mathbf{r} is

$$\mathcal{K} \approx -C_x d\mathbf{r} n(\mathbf{r})^{\frac{4}{3}}. \quad (4.3)$$

Summing the contributions from each cell gives us

$$E_x[n] = -C_x \int d\mathbf{r} n(\mathbf{r})^{\frac{4}{3}}, \quad (4.4)$$

the well known LDA exchange energy.

Thomas-Fermi theory [67–69] makes the local density approximation for the kinetic energy, neglects exchange and correlation completely, and fails miserably. One can attempt to improve the results by using the LDA for exchange and correlation as well, but this does not, unfortunately, solve the problem. Even expanding the results in a gradient expansion is insufficient, although adding derivatives of the density does solve some of the problems. As it turns out, most of the failure in this theory is in the kinetic energy; the LDA is simply unsuited to describing kinetic energy, and something more advanced must be done.

It fell to Kohn and Sham to propose a practical implementation of DFT which was sufficiently accurate that the theory was of use. They proposed to treat the kinetic energy explicitly in some manner. Specifically, they introduced a non-interacting system with the same density as the system of interest, and they then approximated the kinetic energy of the real system, $T[n]$, by the kinetic energy of their non-interacting system, $T_S[n]$. This gives the greater part of the kinetic energy, and they folded the remainder in with the exchange and correlation energy, $E_{xc}[n]$. Thus, the energy in KS-DFT is

$$E[n] = T_S[n] + v_{ext}[n] + E_{Coul}[n] + E_{xc}[n], \quad (4.5)$$

where we have

$$n = \varphi^i \varphi_i, \quad (4.6a)$$

$$T_S[n] = \langle \varphi^i | T | \varphi_i \rangle, \quad (4.6b)$$

$$v_{ext}[n] = \int d\mathbf{r} v_{ext}(\mathbf{r}) n(\mathbf{r}), \quad (4.6c)$$

$$E_{Coul}[n] = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{r_{12}}, \quad (4.6d)$$

and $E_{xc}[n]$ corrects all the errors made in the other terms.

4.2.1 The Kohn-Sham Equations

While we now have a way of extracting the Kohn-Sham energy from a set of orbitals, we need in addition a way of finding the Kohn-Sham orbitals if we are to specify the theory completely. These orbitals are found by solving the Kohn-Sham equations, which bear striking similarity to the Hartree-Fock equations.

The simplest way of deriving the Kohn-Sham equations follows in direct analogy to the derivation of the Hartree-Fock equations. We rewrite the Kohn-Sham energy in terms of the orbitals in as many places as possible, include an Hermitian matrix of Lagrange multipliers which enforce orthonormality, and minimize the resulting Lagrangian

$$\mathcal{L} = h_i^i + \frac{1}{2} g_{ij}^{ij} + E_{xc}[n] - \lambda_i^j (\langle \varphi^i | \varphi_j \rangle - \delta_j^i). \quad (4.7)$$

We must differentiate $E_{xc}[n]$ with respect to the various orbitals; this is done by a functional Taylor series expansion, which gives us

$$\frac{\delta E_{xc}[n]}{\delta \varphi^k(\mathbf{x}_1)} = \int d\mathbf{x}_2 \frac{\delta E_{xc}[n]}{\delta n(\mathbf{x}_2)} \delta(\mathbf{x}_1 - \mathbf{x}_2). \quad (4.8)$$

The functional derivative of E_{xc} with respect to the density is defined to be v_{xc} .

Adding the various terms, we get the Kohn-Sham equations

$$h_S |\varphi_k \rangle = \lambda_k^i |\varphi_i \rangle, \quad (4.9)$$

where

$$h_S = h + J + v_{xc}. \quad (4.10)$$

As is the case with Hartree-Fock theory, we can diagonalize the matrix λ by a unitary transformation of the orbitals. Since the density is invariant to such a transformation, so too is h_S . We thus have the Kohn-Sham equations in their canonical form,

$$h_S |\varphi_k\rangle = \epsilon_k |\varphi_k\rangle, \quad (4.11)$$

where there is no summation to be taken over k . Just as in Hartree-Fock theory, the additional eigenfunctions of the Kohn-Sham operator h_S are the virtual orbitals.

4.2.2 Properties of Kohn-Sham Theory

There are several important properties of the Kohn-Sham orbitals and the associated one-electron Hamiltonian which we would be remiss in not mentioning here. First and foremost it must be emphasized that with the exact v_{xc} , the occupied orbitals give the exact density. Thus, the only terms in the energy which are approximated are the kinetic energy, the exchange energy, and the correlation energy. This is to be contrasted to Hartree-Fock theory, in which every term in the energy is approximated. Thus, in some sense there seems to be more physics built in to the exact Kohn-Sham orbitals, though how this might be utilized is far from clear.

For a given v_{xc} and a given density, note that the only term in the energy expression (4.5) which depends at all on the orbitals is the kinetic energy. This means that in minimizing the energy, we have that the Kohn-Sham orbitals are those which minimize the kinetic energy and yield the exact density. Contrast this to Hartree-Fock orbitals, which minimize the total energy but deliver the wrong density.

Although we have no general Koopmans' theorem for Kohn-Sham orbitals, we do know that the principle ionization potential is the opposite of the highest occupied eigenvalue [70]. This is because at sufficiently large r , the density is dominated by the highest occupied orbital, and matching the known asymptotic forms of the exact density and the Kohn-Sham density informs us that the highest occupied eigenvalue is equal in magnitude but opposite in sign to the exact principle ionization potential.

In addition to these properties of the orbitals, we note two properties of the exchange-correlation potential. First, the exact exchange-correlation potential must properly describe self-exchange, because we have included the self-Coulomb interaction in h_S . Obviously, this term must be cancelled somewhere; in Hartree-Fock theory, this is done by the exchange operator K , and similarly it must be done by v_{xc} in Kohn-Sham theory. This is also true for the exchange-correlation energy, because the Kohn-Sham energy expression includes self-interaction as well.

4.2.3 The Exchange-Correlation Energy

While KS theory has a certain elegant simplicity, it has one major difficulty, in that the exchange-correlation energy $E_{xc}[n]$ is not known except in certain simple cases. Certainly it cannot merely be neglected, as one gets simple Hartree theory if E_{xc} is set to zero. Approximations for it must thus be constructed, which has been one of the major tasks of KS-DFT for several decades now. Considerable progress has been made on the construction of fairly reliable functionals, which has led to KS-DFT being one of the most popular methods for electronic structure calculations at present.

The driving idea behind many functionals is to take the exchange-correlation energy from a model problem which can be solved to high accuracy as a function of the density, and to then fit this function to some form or another, guided by scaling requirements, asymptotic properties, and a whole host of other constraints.

At present, no functional satisfies every constraint, and choices must be made as to which constraints are most important. Often, there will be additional parameters, which are then found by fitting to experiment or to *ab initio* calculations. The most fruitful model problem for our purposes is the HEG, to which we now turn our attention.

4.3 The Homogeneous Electron Gas

The HEG is an important model problem because it can be solved exactly in the Hartree-Fock approximation, allowing us to build a one-matrix and to get functionals for the kinetic energy and the exchange energy which depend only on the density. While these functionals are not of sufficient accuracy, they form the starting point for almost all of modern KS-DFT, and any understanding of our work will require an introduction to this model problem.

Consider, then, a gas of electrons with uniform density n . In order to keep Coulombic repulsions from spreading the system to infinity, we impose a uniform positively charged external potential with the same density. Then the total Hamiltonian is

$$H = T + V_{ext} + V_{ee} + E_b, \quad (4.12)$$

where V_{ext} is now the interaction between the electrons and the uniform positively charged background, and E_b is the energy of the background itself (this is the analogue of the nuclear repulsion energy for a molecule).

We now wish to make the HF approximation, which involves building both the HF energy and the HF Hamiltonian for this system.

For the energy, we replace V_{ee} with $E_{Coul} + E_X$, where E_{Coul} is the Coulomb energy and E_X is the exchange energy (recall that these are not the expectation values of their respective operators). For the Hamiltonian, we replace V_{ee} with $J - K$, where J is the Coulomb operator and K is the exchange operator. Since the HF Hamiltonian is purely electronic, we do not include the term E_b in writing

it. These give us, for the energy and Hamiltonian respectively,

$$E_{HF} = T + E_{ext} + E_{Coul} + E_X + E_b \quad (4.13)$$

and

$$H_{HF} = T + V_{ext} + J - K. \quad (4.14)$$

Now, we can easily see that in both the energy and the Hamiltonian we may cancel the Coulomb contribution with the external potential (the interaction between the electrons and the background, in other words) and the interaction of the background with itself. This is because, writing the electronic density n as n_e and the background density (also equal to n) as n_b for the moment, we have

$$E_{ext} = - \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n_e(\mathbf{r}_1) n_b(\mathbf{r}_2)}{r_{12}} \quad (4.15)$$

$$V_{ext} = - \int d\mathbf{r}_2 \frac{n_b(\mathbf{r}_2)}{r_{12}} \quad (4.16)$$

$$J = \int d\mathbf{r}_2 \frac{n_e(\mathbf{r}_2)}{r_{12}} \quad (4.17)$$

$$E_{Coul} = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n_e(\mathbf{r}_1) n_e(\mathbf{r}_2)}{r_{12}} \quad (4.18)$$

$$E_b = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n_b(\mathbf{r}_1) n_b(\mathbf{r}_2)}{r_{12}}. \quad (4.19)$$

Since $n_e = n_b = n$, the cancellations occur as promised, and the Hamiltonian and energy we must deal with reduce to

$$H_{HF} = T - K \quad (4.20)$$

and

$$E_{HF} = T + E_X. \quad (4.21)$$

If exchange were neglected, the HF spatial orbitals would be simple plane waves,

$$\varphi_{\mathbf{p}}(\mathbf{r}) = (2\pi)^{-3/2} e^{i\mathbf{p}\cdot\mathbf{r}} \quad (4.22)$$

where we have chosen the continuum normalization. We show that plane waves are also eigenfunctions of the exchange operator, and hence are the orbitals we need for the HEG.

Writing the exchange operator acting on a particular orbital $\varphi_p(\mathbf{r}_1)$ and cancelling its normalization constant $(2\pi)^{-3/2}$ for brevity, we have

$$K e^{i\mathbf{p} \cdot \mathbf{r}_1} = \int_{-\mathbf{k}_F}^{\mathbf{k}_F} \frac{d\mathbf{k}}{(2\pi)^3} \int d\mathbf{r}_2 e^{-i\mathbf{k} \cdot \mathbf{r}_2} \frac{P_{12}}{r_{12}} e^{i\mathbf{k} \cdot \mathbf{r}_2} e^{i\mathbf{p} \cdot \mathbf{r}_1}, \quad (4.23)$$

where the integration on \mathbf{k} goes only up to \mathbf{k}_F because the exchange operator consists only of occupied orbitals (that is, $\varphi_{\mathbf{k}_F}$ is the highest occupied orbital of the problem). The action of the permutation operator is of course trivial, so that we have

$$K e^{i\mathbf{p} \cdot \mathbf{r}_1} = \int_{-\mathbf{k}_F}^{\mathbf{k}_F} \frac{d\mathbf{k}}{(2\pi)^3} \int \frac{d\mathbf{r}_2}{r_{12}} e^{-i\mathbf{k} \cdot \mathbf{r}_2 + i\mathbf{k} \cdot \mathbf{r}_1 + i\mathbf{p} \cdot \mathbf{r}_2}. \quad (4.24)$$

In the integration over \mathbf{r}_2 , shift to an integration over \mathbf{r}_{12} , writing $\mathbf{r}_2 = \mathbf{r}_1 - \mathbf{r}_{12}$.

This gives us

$$K e^{i\mathbf{p} \cdot \mathbf{r}_1} = \int_{-\mathbf{k}_F}^{\mathbf{k}_F} \frac{d\mathbf{k}}{(2\pi)^3} \int \frac{d\mathbf{r}_{12}}{r_{12}} e^{i(\mathbf{k}-\mathbf{p}) \cdot \mathbf{r}_{12} + i\mathbf{p} \cdot \mathbf{r}_1}. \quad (4.25)$$

Inserting parentheses to guide the eye, we have

$$K e^{i\mathbf{p} \cdot \mathbf{r}_1} = \left(\int_{-\mathbf{k}_F}^{\mathbf{k}_F} \frac{d\mathbf{k}}{(2\pi)^3} \int \frac{d\mathbf{r}_{12}}{r_{12}} e^{i(\mathbf{k}-\mathbf{p}) \cdot \mathbf{r}_{12}} \right) e^{i\mathbf{p} \cdot \mathbf{r}_1}. \quad (4.26)$$

We thus see that the plane wave $\varphi_p(\mathbf{r})$ is indeed an eigenfunction of the exchange operator, with eigenvalue ϵ_p given by

$$\epsilon_p = \int_{-\mathbf{k}_F}^{\mathbf{k}_F} \frac{d\mathbf{k}}{(2\pi)^3} \int \frac{d\mathbf{r}_{12}}{r_{12}} e^{i(\mathbf{k}-\mathbf{p}) \cdot \mathbf{r}_{12}}. \quad (4.27)$$

These integrals are not difficult, but the result is not illuminating and we will not need it here, so we will not proceed any further. The crucial point is that a plane

wave is a simultaneous eigenfunction of both the kinetic energy and the exchange operators, and is thus an eigenfunction of the Fock operator for the HEG.

Having gotten this far, we can now write the one-matrix for the HEG in the HF approximation. We will also sum over spin here and consider just the spinless one-matrix, for simplicity. This quantity depends only then on spatial coordinates, of course, is suitable for spin unpolarized systems only, and is given by

$$n_1(\mathbf{r}_1, \mathbf{r}_2) = 2 \int_{-\infty}^{k_F} \frac{d\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{r}_{12}}. \quad (4.28)$$

The spin sum accounts for the factor of 2 in the above equation. The angular integrations are trivial, and we have

$$n_1(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\pi^2 r_{12}} \int_0^{k_F} k dk \sin(kr_{12}). \quad (4.29)$$

This last integral is also straightforward, so that we have, making the definition $t = k_F r_{12}$,

$$n_1(\mathbf{r}_1, \mathbf{r}_2) = \frac{k_F^3 \sin(t) - t \cos(t)}{\pi^2 t^3}. \quad (4.30)$$

This can be more compactly expressed as

$$n_1(\mathbf{r}_1, \mathbf{r}_2) = \frac{k_F^3 j_1(t)}{\pi^2 t}, \quad (4.31)$$

where j_1 is a spherical Bessel function of the first kind. (Because spherical Bessel functions appear somewhat frequently in this section, we have included a brief discussion of them in Appendix C.)

We must still determine k_F , which we do by demanding that the diagonal part of the one-matrix is the density; this corresponds to taking the $t = 0$ limit. Doing so gives us simply (see (C.21))

$$n(\mathbf{r}) = \frac{k_F^3}{3\pi^2}, \quad (4.32)$$

or, in other words,

$$n_1(\mathbf{r}_1, \mathbf{r}_2) = 3n(\mathbf{r}) \frac{j_1(t)}{t}. \quad (4.33)$$

Note that we have not specified what precisely the argument of the actual density is; in point of fact, we cannot do so at all, because \mathbf{r}_1 and \mathbf{r}_2 are identical. The natural choice is the center-of-mass vector, $\mathbf{r} = \mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$, which we shall take henceforth. Of course, since we are dealing with the HEG in which the density is a constant, its argument is not particularly relevant in any event.

4.3.1 The Thomas-Fermi Kinetic Energy

Now that we have the HF one-matrix for the HEG (and hence also the HF two-matrix), we can derive both the Thomas-Fermi kinetic energy functional and the Dirac exchange energy functional. For the kinetic energy, we write

$$T = -\frac{1}{4} \int d\mathbf{r}_1 d\mathbf{r}_2 \delta(\mathbf{r}_{12}) (\nabla_1^2 + \nabla_2^2) n_1(\mathbf{r}_1, \mathbf{r}_2), \quad (4.34)$$

which turns out to be a more convenient form than writing the kinetic energy as a single integral. This follows from the string of equalities

$$\langle O \rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \delta(\mathbf{r}_{12}) O(\mathbf{r}_1) n_1(\mathbf{r}_1, \mathbf{r}_2) \quad (4.35)$$

$$= \int d\mathbf{r}_1 d\mathbf{r}_2 \delta(\mathbf{r}_{12}) O(\mathbf{r}_1) n_1^*(\mathbf{r}_2, \mathbf{r}_1) \quad (4.36)$$

$$= \int d\mathbf{r}_1 d\mathbf{r}_2 \delta(\mathbf{r}_{12}) O(\mathbf{r}_2) n_1^*(\mathbf{r}_1, \mathbf{r}_2), \quad (4.37)$$

where in the second line we have used the Hermiticity of the one-matrix and in the last line we have interchanged \mathbf{r}_1 and \mathbf{r}_2 as dummy variables in the integration and used the symmetry of the δ function. Since our one-matrix is purely real, then, we add (4.35) and (4.37) and divide by two, dropping the superfluous complex conjugation and arriving at (4.34) using the kinetic energy operator for O .

If we now make the change of variables in our integration to

$$\left. \begin{aligned} t &= k_F(\mathbf{R}) (\mathbf{r}_1 - \mathbf{r}_2) \\ \mathbf{R} &= \frac{1}{2} (\mathbf{r}_1 + \mathbf{r}_2) \end{aligned} \right\} \iff \left. \begin{aligned} \mathbf{r}_1 &= \mathbf{R} + \frac{1}{2} \mathbf{t} / k_F(\mathbf{R}) \\ \mathbf{r}_2 &= \mathbf{R} - \frac{1}{2} \mathbf{t} / k_F(\mathbf{R}) \end{aligned} \right\} \quad (4.38)$$

we get trivially

$$T = -\frac{1}{4} \int d\mathbf{R} dt \delta(\mathbf{t}) \left(2k_F(\mathbf{R})^2 \nabla_t^2 + \frac{1}{2} \nabla_{\mathbf{R}}^2 \right) 3n(\mathbf{R}) \frac{j_1(t)}{t} \quad (4.39)$$

We can do the integration over t with the aid of the δ function, which gives (with the help of (C.22a) through (C.23) for the derivatives with respect to \mathbf{t})

$$T = \int d\mathbf{R} \left[-\frac{1}{8} \nabla_{\mathbf{R}}^2 n(\mathbf{R}) + \frac{3}{10} n(\mathbf{R}) k_F(\mathbf{R})^2 \right]. \quad (4.40)$$

For the HEG, of course, the density is constant and the derivatives with respect to \mathbf{R} vanish. For any finite system, they do likewise, by the divergence theorem:

$$\int dV \nabla^2 n = \int \nabla n \cdot dS, \quad (4.41)$$

and as we take the surface to infinity, the gradient of the density must decay as at least $r^{-(3+\epsilon)}$ so that the density itself is normalizable. This decay of the density implies that the surface integral vanishes. Thus, the kinetic energy becomes

$$T = \frac{3}{10} \int d\mathbf{R} k_F(\mathbf{R})^2 n(\mathbf{R}). \quad (4.42)$$

4.3.2 The Dirac Exchange Energy

The exchange energy is substantially simpler to derive than the kinetic energy. We begin with the familiar form,

$$E_X = -\frac{1}{4} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n_1(\mathbf{r}_1, \mathbf{r}_2)^2}{r_{12}}, \quad (4.43)$$

where the factor of $\frac{1}{4}$ comes because we have already done the spin sum in our density matrix. As before, we change variables to \mathbf{R} and \mathbf{t} , and doing the angular

integration for t , we have

$$E_X = -\pi \int d\mathbf{R} k_F(\mathbf{R})^{-2} \int_0^\infty t dt n_1(\mathbf{R}, t)^2. \quad (4.44)$$

Inserting the explicit form of our one-matrix, and rewriting k_F in terms of the density in places, we get

$$E_X = -\frac{3}{\pi} \int d\mathbf{R} n(\mathbf{R}) k_F(\mathbf{R}) \int_0^\infty t dt \left(\frac{j_1(t)}{t} \right)^2. \quad (4.45)$$

The integration over t above can be done with the aid of (C.19), and is evaluated in (C.25 - C.26) as $\frac{1}{4}$. Hence the exchange energy is given by the usual Dirac result,

$$E_X = -\frac{3}{4\pi} \int d\mathbf{R} n(\mathbf{R}) k_F(\mathbf{R}). \quad (4.46)$$

4.3.3 Correlation Energy

The correlation energy in the HEG is a much more complicated quantity. One could attempt to approximate it via, for instance, MBPT(2), but this correction diverges, which is certainly unhelpful. More complicated correlation techniques, such as CCSD, are intractable analytically though certainly feasible computationally. The key point is that it has not been possible to write down the exact correlation energy for the HEG in terms of the density, except in certain limiting cases. For practical purposes, one must turn to modeling the correlation energy as a functional of the density.

This is now routine, fortunately. Quantum Monte-Carlo simulations originally performed by Ceperly and Alder have given many points of data, and these data have been fit to functional forms by multiple authors.

4.4 Beyond the Homogeneous Electron Gas

While the local density approximation (LDA) is a quite drastic assumption, it gives remarkably accurate results when the kinetic energy is taken from the Kohn-Sham procedure rather than through the Thomas-Fermi functional. These results are not, unsurprisingly, of sufficient accuracy for atomic and molecular calculations, but they improve over Thomas-Fermi immensely.

These results are encouraging, as they indicate that with the KS construction and with superior functionals, one might reasonably expect to achieve predictive accuracy with KS-DFT. There are, however, several failings which must be overcome by better functionals. While we are not particularly interested here in the details of these failings, the reasons behind them are of more importance to us. Thus, we will discuss some of the problems facing the LDA and ways in which we might solve them.

First, and perhaps most importantly, the LDA has problems handling systems with non-zero spin. This is because it contains no information about the magnetization density, which one might expect is useful in describing spin-polarized systems. Including the magnetization density (or, equivalently, using the densities of both α and β electrons) via the local spin-density approximation (LSDA) alleviates most of the problems for open-shell systems. This is a simple problem with an almost trivial solution, and we shall not comment on it further.

Of greater difficulty is the problem of self-interaction. Although, as we have mentioned, self-interaction must be absent from the exact v_{xc} and E_{xc} , it is not absent in the LSDA. This has manifold implications. For example, the LDA, and even the LSDA, cannot even get the right answer for the hydrogen atom, which is certainly something of an embarrassment. But beyond this, the accumulated error due to self-interaction can become quite large in its own right. Self-interaction error causes the density to have the wrong shape asymptotically because the long-range

Coulomb term is not properly cancelled by equally long-range exchange. This, in turn, means that the band gap is simply awful in the LSDA: the highest occupied eigenvalue is far too high, because it has a large degree of self-repulsion.

Unfortunately, self-interaction is not an easy problem to correct. It is simple enough to make the Fermi-Amaldi correction [71], which takes the form

$$V_{ee}^{FA} = \frac{N-1}{N} V_{ee} \quad (4.47)$$

and makes the LSDA exact for one-electron systems. This is not, of course, a rigorous cancellation of self-interaction. Perdew and Zunger [72] have introduced a self-interaction correction which can be applied to any functional and which alleviates the problem substantially, but one pays the price of having different potentials for different orbitals, which is theoretically unsatisfying at best. The use of exact non-local exchange corrects self-interaction entirely, just as it does in HF theory, but at the price of returning to non-local operators.

A third problem with the LSDA and the LDA is that they tend to describe the chemical bond fairly poorly. Like most approximate DFT methods, they fail badly for weak interactions, and overbind even for stronger interactions.

Finally, the LDA and the LSDA take only local information. It is well known that this is a terrible approximation for the kinetic energy, and one might expect that it is not of wonderful merit for the exchange and correlation energies either. The next logical variable to add is the gradient of the density. This has led to the rise of gradient-corrected functionals and the generalized gradient approximation (GGA), and it is these functionals which have really allowed DFT to be accurate enough for molecular calculations. We will not detail the manifold GGA functionals in existence, but we do wish to note that their success is itself indicative of the errors involved in making the LDA or the LSDA.

4.5 The Exchange-Correlation Hole

Now that the essentials of DFT have been introduced, the relation to wavefunction theory can be explored in some detail. This will be done in the present section. The connection can be made through the two-matrix, for which wavefunction theory provides a prescription and which DFT attempts to model in some way.

4.5.1 A Density Functional Theory Ansatz for the Two-Matrix

Consider the electron-electron interaction energy in DFT. It is written in the form

$$E_{ee} = \frac{1}{2} \int d\mathbf{x}_1 d\mathbf{x}_2 \frac{n(\mathbf{x}_1)n(\mathbf{x}_2)}{r_{12}} + E_X + E_C - T_C. \quad (4.48)$$

Here, T_C is the correction to the Kohn-Sham kinetic energy, which is typically included in the correlation energy functional. We shall return to this point later, but what is important for the moment is that this can be used to define a pair density, or at least a part of the pair density.

Specifically, the Coulomb term comes from writing the pair density as

$$n_2(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{2}n(\mathbf{x}_1)n(\mathbf{x}_2) + \dots \quad (4.49)$$

which suggests that we might wish to model only that part of the pair density which does not contain the Coulomb term. A suggestive form for writing this is

$$n_2(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{2}n(\mathbf{x}_1)n(\mathbf{x}_2)[1 + g_{xc}(\mathbf{x}_1, \mathbf{x}_2)], \quad (4.50)$$

where $1 + g_{xc}$ is the pair correlation function for quantum mechanical electrons and is a symmetric function of its arguments \mathbf{x}_1 and \mathbf{x}_2 .

This form is the simplest and most symmetric form one might wish to write, but it has the disadvantage that certain integral conditions are made less transparent when the pair density is written in this manner. We thus absorb one of the densities into the pair correlation function to define the exchange-correlation hole

[73], via

$$n_2(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{2}n(\mathbf{x}_1)[n(\mathbf{x}_2) + n_{xc}(\mathbf{x}_1, \mathbf{x}_2)]. \quad (4.51)$$

One can try to model the pair correlation function or the exchange-correlation hole directly, and this defines the exchange-correlation energy through

$$E_{ee} = \int d\mathbf{x}_1 d\mathbf{x}_2 \frac{n_2(\mathbf{x}_1, \mathbf{x}_2)}{r_{12}}. \quad (4.52)$$

Obviously, this is not an appealing way to write the energy functional unless the integrations can be done at least in part, as defining the energy through a six-dimensional numerical integral is painful at best. Nonetheless, we have through the exchange-correlation hole a way of modeling the pair density, which simultaneously connects DFT to wavefunction theory and provides a form for the exchange-correlation energy.

4.5.2 Integrations of the Hole

The exchange-correlation hole as written is a little more complicated than it really needs to be, for we can separate the exchange part and the correlation part and model each separately. Doing so, of course, merely defines the exchange hole and the correlation hole individually, with their sum being defined to be the exchange-correlation hole itself. For reference, the exchange hole is defined through

$$n(\mathbf{x}_1)n_x(\mathbf{x}_1, \mathbf{x}_2) = -\frac{1}{2}n_1(\mathbf{x}_1, \mathbf{x}_2)n_1(\mathbf{x}_2, \mathbf{x}_1), \quad (4.53)$$

and the correlation hole is obtained by subtracting the exchange hole from the exchange-correlation hole.

There are some useful integral relations that can be derived with reference to these assorted quantities. We begin with the less obvious and trivial, which we get by demanding that the pair density integrates to the one-matrix with a simple

factor. That is, recalling that

$$n_2(\mathbf{x}_1, \mathbf{x}_2) = \binom{N}{2} \int d\mathbf{X}_{3,N} \Psi^*(\mathbf{X}_{1,N}) \Psi(\mathbf{X}_{1,N}) \quad (4.54)$$

and

$$n(\mathbf{x}_1) = N \int d\mathbf{X}_{2,N} \Psi^*(\mathbf{X}_{1,N}) \Psi(\mathbf{X}_{1,N}) \quad (4.55)$$

we see that

$$n(\mathbf{x}_1) = \frac{2}{N-1} \int d\mathbf{x}_2 n_2(\mathbf{x}_1, \mathbf{x}_2). \quad (4.56)$$

Now suppose that we write the pair density in terms of the exchange-correlation hole as we have done above. Then we have

$$n(\mathbf{x}_1) = \frac{2}{N-1} \int d\mathbf{x}_2 \frac{1}{2} n(\mathbf{x}_1) [n(\mathbf{x}_2) + n_{xc}(\mathbf{x}_1, \mathbf{x}_2)] \quad (4.57)$$

$$= \frac{1}{N-1} n(\mathbf{x}_1) \int d\mathbf{x}_2 [n(\mathbf{x}_2) + n_{xc}(\mathbf{x}_1, \mathbf{x}_2)] \quad (4.58)$$

$$= \frac{1}{N-1} n(\mathbf{x}_1) \left[N + \int d\mathbf{x}_2 n_{xc}(\mathbf{x}_1, \mathbf{x}_2) \right] \quad (4.59)$$

which gives us the sum rule that

$$\int d\mathbf{x}_2 n_{xc}(\mathbf{x}_1, \mathbf{x}_2) = -1. \quad (4.60)$$

This holds trivially for wavefunctions, but is a difficult constraint to impose for arbitrary models for the exchange-correlation hole for many reasons, not the least of which is that it is a constraint for all values of \mathbf{x}_1 . It is often stated that the exchange hole integrates to -1 by itself; this is true in conventional Kohn-Sham theory (where the exchange hole is defined in terms of the Kohn-Sham one-matrix) but is not the case given our definition of the exchange hole, wherein we use the *exact* one-matrix rather than a single determinant approximation thereto.

The other important integration condition on the exchange-correlation hole is simply that it integrates to yield the exchange-correlation energy (and of course the exchange hole and correlation hole integrate respectively to the exchange energy

and the correlation energy) when multiplied by r_{12}^{-1} . These integral conditions are to be satisfied by any method which properly carries out the integration to form the energy from the hole, including the LSDA, CC theory, and so forth.

4.5.3 Averages on the Hole

It may be seen that the exchange-correlation hole gives us a great deal of information about the pair density, but that as a function of six coordinates for each possible spin component, it is a very difficult quantity to model. Furthermore, the only part that is directly relevant for determining the energy is the part which contains information along the interelectronic coordinate. Thus, we define two forms of averaging which allow us to model a simpler quantity that still yields the exact energy. To simplify this discussion, we shall ignore the spin components and work only in spatial coordinates in what follows; the results will hold spin component by spin component.

The first form of averaging in which we will be interested is the spherical average. Here, we write the spatial coordinate of the second electron as

$$\mathbf{r}_2 = \mathbf{r}_1 + \mathbf{u}. \quad (4.61)$$

If we then integrate the exchange-correlation hole over the angular part of the vector \mathbf{u} , we have the spherically averaged hole, *i.e.*,

$$\langle n_{xc}(\mathbf{r}_1, \mathbf{u}) \rangle = \frac{1}{4\pi} \int d\Omega_u n_{xc}(\mathbf{r}_1, \mathbf{r}_1 + \mathbf{u}). \quad (4.62)$$

The factor of $(4\pi)^{-1}$ is present so that the solid angle integration of the spherically averaged hole will equal the solid angle integration of the full hole. Analogous expressions exist, of course, for both the exchange hole and the correlation hole.

The other form of averaging which we will have reason to consider is system averaging. Here, we average instead over the spatial coordinate of the first electron,

weighting by the density. In other words, we have

$$\tilde{n}_{xc}(\mathbf{r}_2) = \frac{1}{N} \int d\mathbf{r}_1 n(\mathbf{r}_1) n_{xc}(\mathbf{r}_1, \mathbf{r}_2). \quad (4.63)$$

Again, the multiplicative factor guarantees that the spherical average integrates to the proper value.

Finally, we can consider the combination of system averaging and spherical averaging,

$$\bar{n}_{xc}(u) = \frac{1}{4\pi N} \int d\mathbf{r}_1 d\Omega_u n(\mathbf{r}_1) n_{xc}(\mathbf{r}_1, \mathbf{r}_1 + \mathbf{u}). \quad (4.64)$$

It is with this quantity that we shall be chiefly concerned. Knowing this averaged hole is sufficient for obtaining the exchange-correlation energy (aside, as always, from the kinetic energy contribution). In terms of the various averaged holes, we have the sum rule

$$4\pi \int_0^\infty u^2 du \bar{n}_{xc}(u) = -1 \quad (4.65)$$

and the following associated energy integrals:

$$\frac{1}{2} 4\pi N \int_0^\infty u^2 du \frac{\bar{n}_{xc}(u)}{u} = E_{XC} - T_C \quad (4.66)$$

$$\frac{1}{2} 4\pi N \int_0^\infty u^2 du \frac{\bar{n}_x(u)}{u} = E_X \quad (4.67)$$

$$\frac{1}{2} 4\pi N \int_0^\infty u^2 du \frac{\bar{n}_c(u)}{u} = E_C - T_C. \quad (4.68)$$

4.5.4 Kinetic Energy Corrections

One will note that in the foregoing, we have explicitly separated out the kinetic energy correction T_C , since we are interested in correcting the short-range electronic interaction. In most DFT literature, the kinetic correction is included in the exchange-correlation hole by the use of the adiabatic connection formalism.

Since we will need to remove this component, we discuss the adiabatic connection [74–77] here.

Although there are a number of subtleties which we will not mention, the essential idea of the adiabatic connection technique is straightforward enough that we will sketch it here. We begin by making the definition

$$E_\lambda = \langle \Psi_\lambda | T + V_{ext} + \lambda V_{ee} | \Psi_\lambda \rangle, \quad (4.69)$$

where $|\Psi_\lambda\rangle$ is that wavefunction which minimizes E_λ subject to the constraint that the density it yields is the same as the density at $\lambda = 1$ (it in this constraint that most of the subtleties arise). Note that at $\lambda = 1$, $E_{\lambda=1}$ is the exact energy, and at $\lambda = 0$, $E_{\lambda=0}$ becomes $T_S + V_{ext}$. This latter follows because at $\lambda = 0$, the Hamiltonian contains only one-electron operators so that the wavefunction is a single determinant, and the minimization becomes a minimization only of the kinetic energy, so that $|\Psi_{\lambda=0}\rangle = |\Phi_{KS}\rangle$. Thus, we have

$$E_{\lambda=1} - E_{\lambda=0} = (T - T_S) + E_{ee} = E_{xc} + E_{Coul}. \quad (4.70)$$

However, we can also write this difference as

$$E_{\lambda=1} - E_{\lambda=0} = \int_0^1 d\lambda \frac{d}{d\lambda} E_\lambda, \quad (4.71)$$

which becomes, using the Hellman-Feynman theorem,

$$E_{\lambda=1} - E_{\lambda=0} = \int_0^1 d\lambda \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle. \quad (4.72)$$

Thus, we can write the exchange-correlation energy as

$$E_{xc} = \int_0^1 d\lambda \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle - E_{Coul}. \quad (4.73)$$

In terms of the exchange-correlation hole, this is just

$$E_{xc} = \frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1) n_{xc}^\lambda(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}, \quad (4.74)$$

where n_{xc}^λ is the exchange-correlation hole at coupling constant λ .

The key point is that the exchange-correlation hole we have dealt with so far corresponds to that of the fully interacting system. If we are willing to calculate it for all values of the coupling constant λ , we can then define the coupling constant average of the exchange-correlation hole as

$$\hat{n}_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \int_0^1 d\lambda n_{xc}^\lambda(\mathbf{r}_1, \mathbf{r}_2). \quad (4.75)$$

If we insert this into our equations above in place of the usual exchange-correlation hole, then the kinetic energy correction is also included.

4.5.5 The Relation to Intracules

It should be fairly clear that the system-averaged, spherically averaged exchange-correlation hole is intimately related to the position intracule. We recall that the latter is defined by

$$P(u) = \int d\mathbf{x}_1 d\mathbf{x}_2 \delta(r_{12} - u) n_2(\mathbf{x}_1, \mathbf{x}_2). \quad (4.76)$$

In contrast, by combining (4.51) and (4.64), the system-averaged, spherically averaged exchange-correlation hole can be written as

$$\bar{n}_{xc}(u) = \frac{1}{4\pi N} \int d\mathbf{x}_1 d\mathbf{x}_2 \frac{\delta(r_{12} - u)}{u^2} [2n_2(\mathbf{x}_1, \mathbf{x}_2) - n(\mathbf{x}_1)n(\mathbf{x}_2)]. \quad (4.77)$$

Simple algebra thus tells us that

$$\bar{n}_{xc}(u) = \frac{1}{2\pi u^2 N} P(u) - \int d\mathbf{x}_1 d\mathbf{x}_2 \frac{n(\mathbf{x}_1)n(\mathbf{x}_2)}{4\pi N} \frac{\delta(r_{12} - u)}{u^2}. \quad (4.78)$$

To put this on a more physical and less mathematical footing, the position intracule tells us the probability that two-electrons are found a distance u apart. We can define a Coulomb intracule as

$$P_{Coul}(u) = \frac{1}{2} \int d\mathbf{x}_1 d\mathbf{x}_2 \delta(r_{12} - u) n(\mathbf{x}_1) n(\mathbf{x}_2), \quad (4.79)$$

which provides the same information assuming that the electrons are classical non-interacting particles. Then the system-averaged, spherically averaged exchange-correlation hole tells us about the corrections to the probability that two electrons are a distance u apart due to the fact that the electrons interact quantum mechanically. A model for the exchange-correlation hole, with the appropriate averages, is thus essentially just a model for the position intracule.

CHAPTER 5

A NEW MODEL FOR THE CORRELATION HOLE

Now that we have developed the requisite theoretical tools, we may proceed with our proposed solution for the cusp problem. This solution is implemented as a model for the correlation hole, and we will begin by presenting the basic idea before proceeding with the development.

5.1 Separations of the Correlation Hole

The correlation hole, as we have seen, contains sufficient information to specify the correlation energy. It is therefore the central quantity of interest for our purposes: an accurate but basis set insensitive model for the correlation hole would deliver an accurate but basis set insensitive model for the correlation energy, which is our goal.

Because the correlation cusp has only a short-range effect on the wavefunction, it has only a short-range effect on the correlation hole as well. The longer range component of the correlation hole, therefore, should converge rapidly with respect to basis set size, and only the short-range part should be particularly sensitive to the underlying basis. Therefore, if we seek a model for the correlation hole which is both reasonably accurate and reasonably insensitive to the one-particle basis, we need only treat the short-range component in a more general way than is done in traditional wavefunction theory. To this end, we write

$$\bar{n}_c(u) = \bar{n}_c^{SR}(u)f(u) + \bar{n}_c^{LR}(u)[1 - f(u)], \quad (5.1)$$

where $f(u)$ is some cutoff function which must be short-ranged and $\bar{n}_c^{SR}(u)$ and $\bar{n}_c^{LR}(u)$ are the short- and long-range parts of the correlation hole, the latter to be treated within the context of standard wavefunction theory.

Such a separation is not new; Perdew and coworkers make this separation in defining the RPA+ model [78], and Savin and his collaborators have done the same in their own efforts towards solving this problem [79]. We feel that this approach is sufficiently flexible and general to warrant further investigation despite the prior work in the area.

We are left with the task of determining a short-range model for the correlation hole, without which our proposed separation is useless. Fortunately, the LDA correlation hole is known to be reasonably accurate at short-range [80, 81], and we will use Perdew and Wang's parameterization of the HEG correlation hole [82] for our short-range model. It is to this parameterization which we turn our attention for the moment.

5.2 The Perdew-Wang Electron Gas Correlation Hole

In their 1991 paper, Perdew and Wang parameterize the pair-distribution function for an HEG of density n , albeit the coupling-constant averaged pair-distribution function. Thus, the correlation hole which one might build from their model includes the correlation corrections to the kinetic energy. We must remove these effects, but this can fortunately be done in the following manner.

The coupling-constant averaged pair-distribution function, \bar{g} , may be written in terms of the bare pair-distribution function g as

$$\bar{g}\left(\frac{\hbar^2}{m_e e^2}\right) = \frac{1}{e^2} \int_0^{e^2} d\lambda g\left(\frac{\hbar^2}{m_e \lambda}\right), \quad (5.2)$$

where we have retained factors of \hbar and so forth for clarity; the argument of the pair-distribution function represents an average length, and is at full coupling-constant equal to the Bohr radius a_0 .

Let us now multiply (5.2) by e^2 and then differentiate both sides with respect to e^2 . The left-hand side becomes

$$\frac{\partial}{\partial e^2} e^2 \bar{g} \left(\frac{\hbar^2}{m_e e^2} \right) = \left(1 + e^2 \frac{\partial}{\partial e^2} \right) \bar{g} \left(\frac{\hbar^2}{m_e e^2} \right), \quad (5.3)$$

while the right-hand side becomes

$$\frac{\partial}{\partial e^2} \int_0^{e^2} d\lambda g \left(\frac{\hbar^2}{m_e \lambda} \right) = g \left(\frac{\hbar^2}{m_e e^2} \right). \quad (5.4)$$

Equating the two, then, allows us to write

$$g(a_0) = \left(1 + e^2 \frac{\partial}{\partial e^2} \right) \bar{g}(a_0) = \left(1 - a_0 \frac{\partial}{\partial a_0} \right) \bar{g}(a_0), \quad (5.5)$$

where we have used the fact that the only dependence on e^2 is through the Bohr radius.

The upshot of all of this is that if we know the dependence of the pair-distribution function on the Bohr radius, we can extract the bare pair-distribution function through simple differentiation. The Bohr radius, however, is only one parameter in the pair-distribution function. For reference, we will introduce the other parameters on which g depends before giving the PW parameterization.

5.2.1 Parameters in the Electron Gas Pair-Distribution Function

The most important parameter is the Wigner-Seitz radius r_s , a dimensionless parameter characterizing the average distance between electrons; it is given by

$$\frac{4}{3} \pi r_s^3 = \frac{1}{a_0^3 n}, \quad (5.6)$$

where of course n is the density. Since r_s and the Bohr radius a_0 are inversely proportional to each other, we have

$$-a_0 \frac{\partial}{\partial a_0} = r_s \frac{\partial}{\partial r_s}, \quad (5.7)$$

and hence we rewrite (5.5) as

$$g(a_0) = \left(1 + r_s \frac{\partial}{\partial r_s}\right) \bar{g}(a_0). \quad (5.8)$$

A second density parameter is the Fermi wave-vector k_F , defined through

$$k_F^3 = 3\pi^2 n, \quad (5.9)$$

so that the product $k_F r_s$ is a constant; specifically,

$$(k_F r_s a_0)^3 = \frac{9\pi}{4}. \quad (5.10)$$

The length scale of the HEG correlation hole is set by the Thomas-Fermi screening wave vector,

$$k_S = \left(\frac{4k_F}{\pi a_0}\right)^{\frac{1}{2}} = \kappa r_s^{\frac{1}{2}} k_F, \quad (5.11)$$

where the constant κ is

$$\kappa = \left(\frac{16}{3\pi^2}\right)^{\frac{1}{3}}. \quad (5.12)$$

Spin polarization must be taken into account if we are to describe open-shell systems, for which purpose we define a spin-polarization parameter ζ as

$$\zeta = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow}. \quad (5.13)$$

Here, n_\uparrow (n_\downarrow) is the density of spin-up (spin-down) electrons; their sum is hence the total density. We can use ζ to define a factor which accounts for the changes in length scales due to spin-polarization. This factor, $\phi(\zeta)$, is given by

$$\phi(\zeta) = \frac{(1 + \zeta)^{\frac{2}{3}} + (1 - \zeta)^{\frac{2}{3}}}{2}. \quad (5.14)$$

Finally, recalling that the electron-electron separation is u , we can combine these various parameters to define a pair of normalized interelectronic distances,

$$v = \phi k_S u \quad (5.15)$$

and

$$t = k_F u. \quad (5.16)$$

Now that we have defined all the relevant parameters, we can introduce the PW parameterization.

5.2.2 The Perdew-Wang Parameterization of the Electron Gas Pair-Distribution Functions

Perdew and Wang find the long-range part of the correlation contribution to the coupling-constant averaged pair-distribution function to be

$$\bar{g}_c^{LR} = \frac{\phi^3 r_s \bar{f}_1(v)}{\kappa t^2}, \quad (5.17)$$

where $\bar{f}_1(v)$ will be defined momentarily and \bar{g}_c is the correlation contribution to the coupling-constant averaged pair-distribution function. The function $\bar{f}_1(v)$ is unknown, but can be described well by the Padé approximant

$$\bar{f}_1(v) = \frac{a_1 + a_2 v + a_3 v^2}{1 + b_1 v + b_2 v^2 + b_3 v^3 + b_4 v^4}, \quad (5.18)$$

where the coefficients are $a_1 = -0.1244$, $a_2 = 0.027032$, $a_3 = 0.0024317$, $b_1 = 0.2199$, $b_2 = 0.086664$, $b_3 = 0.012858$, and $b_4 = 0.0020$. Note the typographical error in the original reference, in which a_3 is incorrect [83]. The Padé form above is accurate only for $v > 1$, and the short-range part must therefore be handled separately.

In order to describe this short-range part, Perdew and Wang introduce a second function \bar{f}_2 as the product of a power series and a Gaussian cutoff; it is given explicitly by

$$\bar{f}_2 = [-a_1 - (a_2 - a_1 b_1)v + c_1 v^2 + c_2 v^3 + c_3 v^4 + c_4 v^5] e^{-\frac{d(\zeta)}{\phi^2} t^2}, \quad (5.19a)$$

$$= \mathcal{P} e^{-\frac{d(\zeta)}{\phi^2} t^2}, \quad (5.19b)$$

where $d(\zeta)$ is in principle arbitrary. It is found, however, that $d(\zeta) = 0.305 - 0.136\zeta^2$ gives good agreement with the Monte-Carlo data of Ceperly and Alder, so we use this for $d(\zeta)$ henceforth.

The first two coefficients in the power series compensate for the $v = 0$ divergences in \bar{f}_1 . Insisting that the model for \bar{g}_c give the correct HEG value at $u = 0$ fixes c_1 , giving

$$c_1 = (a_1 b_2 + a_2 b_1 - a_3 - a_1 b_1^2) - a_1 p + \frac{1 - \zeta^2}{2\kappa r_s^2 \phi^5} (F_1 - 1), \quad (5.20)$$

where

$$F_1 = \frac{1 + 0.193r_s}{1 + 0.525r_s + 0.101325r_s^2} \quad (5.21)$$

and $p = d(\zeta)/(\kappa^2 r_s \phi^4)$ so that $pv^2 = d(\zeta)\phi^{-2}t^2$. Similarly, insisting that the slope be correct at the origin fixes c_2 to be

$$c_2 = (a_1 b_3 - 2a_1 b_1 b_2 + a_2 b_2 + a_3 b_1 - a_2 b_1^2 + a_1 b_1^3) - (a_2 - a_1 b_1)p + \pi \frac{1 - \zeta^2}{8\phi^6 r_s^{\frac{3}{2}}} F_1 F_2, \quad (5.22)$$

where

$$F_2 = \frac{1 + 0.3393r_s}{2 + 0.9r_s + 0.10161r_s^2}. \quad (5.23)$$

The remaining coefficients c_3 and c_4 are determined so that the model correlation hole satisfies the sum rule

$$\int d\mathbf{u} n \bar{g}_c = 0 \quad (5.24)$$

and yields the correct correlation energy density ϵ_c , so that

$$\frac{1}{2} e^2 \int d\mathbf{u} \frac{n \bar{g}_c}{u} = \frac{e^2}{a_0} \epsilon_c. \quad (5.25)$$

This gives us a pair of linear equations in the unknowns c_3 and c_4 , the solutions of which are

$$c_3 = 0.10847p^{\frac{5}{2}} + 1.4604p^2 + 0.51749p^{\frac{3}{2}} - 3.5297c_1 p - 1.9030c_2 p^{\frac{1}{2}} + 1.0685p^2 \ln p + 34.356\phi^{-3}p^2 \epsilon_c \quad (5.26)$$

and

$$\begin{aligned} c_4 = & -0.081593p^3 - 1.0810p^{\frac{5}{2}} - 0.31677p^2 + 1.9030c_1p^{\frac{3}{2}} \\ & + 0.76485c_2p - 0.71019p^{\frac{5}{2}} \ln p - 22.836\phi^{-3}p^{\frac{5}{2}}\epsilon_c. \end{aligned} \quad (5.27)$$

In order to completely specify the model, we must still give a form for ϵ_c .

Fortunately, Perdew and Wang have provided this as well [84], although this is not the only parameterization available. We choose to work with their parameterization for the sake of consistency. The Perdew Wang parameterization is

$$\epsilon_c(r_s, \zeta) = \epsilon_c(r_s, 0) + \alpha_c(r_s) \frac{\varphi(\zeta)}{\varphi''(0)} (1 - \zeta^4) + [\epsilon_c(r_s, 1) - \epsilon_c(r_s, 0)] \varphi(\zeta) \zeta^4, \quad (5.28)$$

where

$$\varphi(\zeta) = \frac{(1 + \zeta)^{\frac{4}{3}} + (1 - \zeta)^{\frac{4}{3}} - 2}{2^{\frac{4}{3}} - 2} \quad (5.29)$$

and hence $\varphi''(0) = \frac{8}{9} \frac{1}{2^{\frac{4}{3}} - 2}$. The functions $\epsilon_c(r_s, 0)$, $\epsilon_c(r_s, 1)$, and $\alpha_c(r_s)$ are all fit to the form

$$G(r_s) = -2A(1 + \alpha_1 r_s) \ln(1 + \mathcal{F}^{-1}), \quad (5.30)$$

where

$$\mathcal{F} = 2A(\beta_1 r_s^{\frac{1}{2}} + \beta_2 r_s + \beta_3 r_s^{\frac{3}{2}} + \beta_4 r_s^2). \quad (5.31)$$

In Table 5–1, we give the parameters for the three functions.

Table 5–1: Parameters defining ϵ_c for the HEG

	$\epsilon_c(r_s, 0)$	$\epsilon_c(r_s, 1)$	$-\alpha_c(r_s)$
A	0.031091	0.015545	0.016887
α_1	0.21370	0.20548	0.028829
β_1	7.5957	14.1189	10.357
β_2	3.5876	6.1977	3.6231
β_3	1.6382	3.3662	0.47990
β_4	0.49294	0.62517	0.12279

Adapted from J.P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992), Table I, page 13246.

With all these quantities now defined, the Perdew-Wang model for the correlation part of the coupling-constant averaged pair-distribution function of an

HEG is

$$\bar{g}_c = \frac{\phi^3 r_s [\bar{f}_1(v) + \bar{f}_2]}{\kappa t^2}. \quad (5.32)$$

Note that there is, in fact, an energetically unimportant long-range oscillation which has been smoothed out in their model, and which we are not interested in since we wish to use only the short-range part in any event.

5.2.3 Removing the Coupling-Constant Average

Our task is to differentiate the PW form specified in the previous subsection with respect to the Wigner-Seitz radius, so that we may undo the coupling-constant average. This is facilitated somewhat by noting that

$$r_s \frac{\partial}{\partial r_s} = \frac{1}{2} v \frac{\partial}{\partial v} = -p \frac{\partial}{\partial p}. \quad (5.33)$$

Clearly, then, we have

$$r_s \frac{\partial \bar{g}_c}{\partial r_s} = \bar{g}_c + \frac{\phi^3 r_s}{\kappa t^2} \left[\frac{1}{2} v \frac{\partial \bar{f}_1(v)}{\partial v} + e^{-pv^2} r_s \frac{\partial \mathcal{P}}{\partial r_s} \right]. \quad (5.34)$$

Differentiation of $\bar{f}_1(v)$ is straightforward, and the result is best written as

$$\frac{1}{2} v \frac{\partial \bar{f}_1(v)}{\partial v} = \frac{v}{2} \frac{a_2 + 2a_3 v - \bar{f}_1(v)(b_1 + 2b_2 v + 3b_3 v^2 + 4b_4 v^3)}{1 + b_1 v + b_2 v^2 + b_3 v^3 + b_4 v^4}. \quad (5.35)$$

Similarly, differentiating \mathcal{P} gives us

$$\begin{aligned} r_s \frac{\partial \mathcal{P}}{\partial r_s} = & -\frac{1}{2}(a_2 - a_1 b_1)v + 2c_1 v^2 + \frac{3}{2} c_2 v^3 + 2c_3 v^4 + \frac{5}{2} c_4 v^5 \\ & + v^2(r_s c'_1) + v^3(r_s c'_2) + v^4(r_s c'_3) + v^5(r_s c'_4). \end{aligned} \quad (5.36)$$

The differentiation of the coefficients c_i is a bit tedious but not difficult. We have

$$r_s c'_1 = a_1 p - \frac{1 - \zeta^2}{\kappa r_s^2 \phi^5} (F_1 - 1) + \frac{1 - \zeta^2}{2 \kappa r_s \phi^5} \frac{\partial F_1}{\partial r_s}, \quad (5.37)$$

where

$$\frac{\partial F_1}{\partial r_s} = \frac{0.193 - 0.525(1 + 0.386 r_s) F_1}{1 + 0.193 r_s} F_1. \quad (5.38)$$

Likewise, we get

$$r_s c'_2 = (a_2 - a_1 b_1)p - 3\pi \frac{1 - \zeta^2}{r_s^{\frac{3}{2}} \phi^6} F_1 F_2 + \frac{\pi}{8} \frac{1 - \zeta^2}{r_s^{\frac{1}{2}} \phi^6} (F'_1 F_2 + F_1 F'_2), \quad (5.39)$$

where

$$\frac{\partial F_2}{\partial r_s} = \frac{0.3393 - (0.9 + 0.20322 r_s) F_2}{1 + 0.3393 r_s} F_2. \quad (5.40)$$

For c_3 , we have

$$\begin{aligned} r_s c'_3 = & -0.271175 p^{\frac{5}{2}} - 3.9893 p^2 - 0.776235 p^{\frac{3}{2}} + 3.5297(c_1 - r_s c'_1)p \\ & + 0.9515(c_2 - 2r_s c'_2)p^{\frac{1}{2}} - 2.137p^2 \ln p + 34.356\phi^{-3}(r_s \epsilon'_c - 2\epsilon_c)p^2, \end{aligned} \quad (5.41)$$

where we will postpone defining the derivative of ϵ_c until after we define the derivative of c_4 . This latter is given by

$$\begin{aligned} r_s c'_4 = & 0.244788 p^3 + 3.41269 p^{\frac{5}{2}} + 0.63354 p^2 + 1.9030(r_s c'_1 - \frac{3}{2}c_1)p^{\frac{3}{2}} \\ & + 0.76485(r_s c'_2 - c_2)p + 1.775475 p^{\frac{5}{2}} \ln p - 22.836\phi^{-3}(r_s \epsilon'_c - \frac{5}{2}\epsilon_c)p^{\frac{5}{2}}. \end{aligned} \quad (5.42)$$

Our one remaining task to is to specify $r_s \epsilon'_c$; in order to do so, we need to differentiate G . This derivative is

$$r_s G' = r_s \left(\frac{\alpha_1}{1 + \alpha_1 r_s} G + \frac{2A(1 + \alpha_1 r_s)}{\mathcal{F}(1 + \mathcal{F})} \mathcal{F}' \right) \quad (5.43)$$

with

$$\mathcal{F}' = A(\beta_1 + 2\beta_2 r_s^{\frac{1}{2}} + 3\beta_3 r_s + 4\beta_4 r_s^{\frac{3}{2}}) r_s^{-\frac{1}{2}}. \quad (5.44)$$

Thus, we have

$$r_s \epsilon'_c = r_s \epsilon_c(r_s, 0)' + r_s \alpha_c(r_s)' \frac{\varphi(\zeta)}{\varphi(0)''} (1 - \zeta^4) + [r_s \epsilon_c(r_s, 1)' - r_s \epsilon_c(r_s, 0)'] \varphi(\zeta) \zeta^4, \quad (5.45)$$

where for each of the above derivatives we use (5.43) with the appropriate parameters. Combining everything, we end up with

$$g_c = 2\bar{g}_c + \frac{\phi^3 r_s}{\kappa t^2} \left[\frac{1}{2} v \frac{\partial \bar{f}_1(v)}{\partial v} + e^{-pv^2} r_s \frac{\partial \mathcal{P}}{\partial r_s} \right], \quad (5.46)$$

where we make use of (5.35 - 5.45) in handling the derivatives.

If we now wish to treat non-homogeneous systems within the local spin density approximation (LSDA), we define a correlation hole as

$$n_c^{LSDA}(\mathbf{R}, u) = n(\mathbf{R})g_c(u; n(\mathbf{R})), \quad (5.47)$$

where we have noted that all density parameters in g_c are to be taken as coming from the density at the point of interest. This hole is already spherically symmetric, so n_c is the same as its spherical average. The system averaged, spherically averaged LSDA correlation hole is thus just

$$\bar{n}_c(u) = \frac{1}{N} \int d\mathbf{R} n(\mathbf{R})^2 g_c(u; n(\mathbf{R})). \quad (5.48)$$

It is this quantity which we will wish to use as the short-range component of the correlation hole in the separation of (5.1).

5.3 Gradient Corrections

While what we have discussed so far has the great advantage of simplicity, the approximation of a molecule as being locally a homogeneous electron gas is a severe one, and we would like to include corrections in the form of dependence on the density gradient. Such corrections have, of course, a long history in DFT, although it is uncommon to see them applied at the level of the correlation hole. Nevertheless, Perdew, Burke, and Wang (PBW) have given a prescription for adding gradient corrections to the LDA correlation hole [85], and we can simply take their form and apply the same manipulations we have just carried out in order to find a gradient corrected but not coupling constant averaged correlation hole. In order to do so, we need to define one additional parameter, a reduced density gradient given by

$$s = \frac{\|\nabla n\|}{2k_F n}. \quad (5.49)$$

In terms of the new variable s , the PBW gradient correction to the hole is

$$\delta\bar{g}_c = \frac{\phi(\zeta)^3 k_F^2 s^2}{a_0 n} B_c, \quad (5.50)$$

where

$$B_c = \frac{1 - e^{-pv^2}}{18\pi^3(1 + \frac{1}{12}v^2)^2} + \frac{2p^2}{3\pi^3} [1 - E_1(12p)] v^2 e^{-pv^2}. \quad (5.51)$$

Here, $E_1(x)$ is defined as

$$E_1(x) = xe^x \int_x^\infty \frac{dt}{t} e^{-t}. \quad (5.52)$$

Note that in the PBW reference, atomic units are used, so that the factor of the Bohr radius in (5.50) is missing, and also that there is an error in equation 51 of that reference, in which $2p^2/3\pi^2$ should be $2p^2/3\pi^3$, as we have used [83]. It proves convenient to break B_c into a short-range part and a long-range part, as

$$B_c = B_c^{SR} + B_c^{LR} \quad (5.53a)$$

$$B_c^{SR} = \frac{2pv^2}{3\pi^3} [1 - E_1(12p)] pe^{-pv^2} \quad (5.53b)$$

$$B_c^{LR} = \frac{1 - e^{-pv^2}}{18\pi^3(1 + \frac{1}{12}v^2)^2}. \quad (5.53c)$$

If we now apply the operator $1 - a_0 \frac{\partial}{\partial a_0}$ to (5.50), we get

$$\delta g_c = \frac{\phi(\zeta)^3 k_F^2 s^2}{a_0 n} \left(2 - a_0 \frac{\partial}{\partial a_0} \right) B_c. \quad (5.54)$$

Recalling that we may replace the derivative with respect to a_0 with derivatives with respect to p and v , we may write the above instead as

$$\delta n_c = \phi(\zeta)^3 k_F^2 s^2 \left(2 + \frac{1}{2}v \frac{\partial}{\partial v} - p \frac{\partial}{\partial p} \right) (B_c^{SR} + B_c^{LR}), \quad (5.55)$$

where we have moved the density from the denominator of the right-hand side over to the left-hand side and used the fact that $n_c = ng_c$.

Let us first differentiate the long-range part of B_c , recalling that the derivatives of any function of pv^2 cancel exactly. We thus have

$$\left(2 + \frac{1}{2}v\frac{\partial}{\partial v} - p\frac{\partial}{\partial p}\right) B_c^{LR} = \frac{1 - e^{-pv^2}}{18\pi^3} \left(2 + \frac{1}{2}v\frac{\partial}{\partial v}\right) (1 + \frac{1}{12}v^2)^{-2} \quad (5.56a)$$

$$= \frac{1 - e^{-pv^2}}{9\pi^3(1 + \frac{1}{12}v^2)^3}. \quad (5.56b)$$

Similarly, the short-range part of B_c can be done as

$$\left(2 + \frac{1}{2}v\frac{\partial}{\partial v} - p\frac{\partial}{\partial p}\right) B_c^{SR} = \frac{2pv^2}{3\pi^3} e^{-pv^2} \left(2 - p\frac{\partial}{\partial p}\right) p [1 - E_1(12p)] \quad (5.57a)$$

$$= \frac{2p^2v^2}{3\pi^3} e^{-pv^2} (1 - 12p [1 - E_1(12p)]). \quad (5.57b)$$

Thus, the gradient correction to the correlation hole is given by

$$\delta n_c = \phi(\zeta)^3 k_F^2 s^2 \left[\frac{1 - e^{-pv^2}}{9\pi^3(1 + \frac{1}{12}v^2)^3} + \frac{2p^2v^2}{3\pi^3} e^{-pv^2} (1 - 12p [1 - E_1(12p)]) \right]. \quad (5.58)$$

5.4 The Cutoff Function

While we have defined a short-range component of the correlation hole, we cannot consider the separation of (5.1) to specify a model until we consider the cutoff function $f(u)$. The cutoff function must, of course, be short in range, lest the improper longer-range behavior of the LDA correlation hole manifest itself. For small u , it should have the series expansion

$$f(u) = 1 + \mathcal{O}(u^2) \quad (5.59)$$

so that we get the full benefit of the accurate on-top hole and on-top slope given by the LDA (we wish, in other words, the hole at $u = 0$ to be the LDA hole, and the slope at $u = 0$ to be the LDA slope). The cutoff function should probably be system dependent, and certainly it should depend on the basis set used in the wavefunction part of the calculation as well as on the level of correlation. The

correlation hole we build, finally, should satisfy the integration constraint of (4.65) when combined with the exchange hole given by our wavefunction.

In order to satisfy these criteria, we will initially use

$$f(u) = e^{-\alpha u^2}, \quad (5.60)$$

where α is chosen so that the sum rule is satisfied to some desired accuracy. Satisfaction of the sum rule will create dependence on the basis set, level of correlation, and system being treated.

However, we will not wish to actually build the correlation hole, as doing so is sufficiently difficult and time consuming that we could instead choose to use a larger basis set and achieve results of the same quality as with our model in a smaller basis set. To this end, we wish to model the cutoff parameter α in some way which has functional dependence on the density (and possibly its gradients) and on the basis set and level of correlation. Such a model will be deferred until Chapter 7, however.

5.5 Connections to Other Correction Techniques

Our proposal is another in a long line of ideas geared towards avoiding the difficulties associated with using a one-particle basis set, and it may prove helpful to sketch the relation of our proposal to some of the other ideas.

The connections to the explicitly correlated R12 methods of Kutzelnigg and coworkers is only in that both they and we are interested in the same general problem, and that both they and we worry only about changing the description of correlation to account for the effects of Kato's cusp condition on the short-range correlation.

More obvious, perhaps, is the connection to the transcorrelated Hamiltonian approach and to the various effective potential methods. Recall that the transcorrelated Hamiltonian procedure generates a screened electron interaction potential

(which is the effect introduced by our cutoff function applied to the wavefunction part of the correlation hole) and then corrects for the screening with three-body terms and two-body momentum terms, while effective potential methods screen the electron interaction potential but do not correct this approximation. Our scheme may be seen as related to the transcorrelated approach, approximated in such a way that the complicated additional terms are replaced by a simple one-body term from the HEG. At the cost of rigor, it should allow us to carry out reasonably accurate CC calculations without the need for either very large basis sets or considerable numbers of new integrals. In addition, the correlation energy, written as it would be in terms of a CC part and a DFT part, could be easily differentiated, and since the terms which give rise to the complications for evaluating properties in the usual transcorrelated approach are approximated, we should have minimal difficulty in the treatment of properties.

5.6 The Proposed Implementation

Apart from specifying the precise functional form of the cutoff function $f(u)$, we have now provided a complete model for the correlation hole from a given wavefunction. In this section, we will discuss how such a model might be implemented in such a way as to be efficient and flexible. First, however, we should write the total energy functional for our usual Hamiltonian with this modified correlation hole.

Recall that the total energy can be written as

$$E = \gamma_p^q h_q^p + \Gamma_{pq}^{rs} g_{rs}^{pq} \quad (5.61)$$

with h_q^p being the matrix elements of the one-particle parts of the Hamiltonian. The two-matrix Γ decomposes as we have seen into pieces which yield the

Coulomb, exchange, and correlation energies, these pieces being respectively

$$(\Gamma_{pq}^{rs})_{Coul} = \frac{1}{2}\gamma_p^r\gamma_q^s, \quad (5.62a)$$

$$(\Gamma_{pq}^{rs})_{exch} = -\frac{1}{2}\gamma_p^s\gamma_q^r, \quad (5.62b)$$

$$(\Gamma_{pq}^{rs})_{corr} = -\frac{1}{2}\bar{\gamma}_p^{[r}\bar{\gamma}_q^{s]} + \bar{\Gamma}_{pq}^{rs} = \Gamma_{pq}^{rs} - \frac{1}{2}\gamma_p^{[r}\gamma_q^{s]} \equiv \Xi_{pq}^{rs}. \quad (5.62c)$$

Thus, the total energy is

$$E = \gamma_p^q h_q^p + \Gamma_{pq}^{rs} g_{rs}^{pq} + E_{cusp} \quad (5.63)$$

The cusp energy, writing $\mathcal{V}(u)$ for $f(u)/u$, is

$$E_{cusp} = -\Xi_{pq}^{rs} \mathcal{V}_{rs}^{pq} + \frac{1}{2}4\pi N \int_0^\infty u^2 du \mathcal{V}(u) \bar{n}_c^{LDA}(u), \quad (5.64)$$

The total energy from our model is therefore

$$E = \gamma_p^q h_q^p + \Gamma_{pq}^{rs} g_{rs}^{pq} - \Xi_{pq}^{rs} \mathcal{V}_{rs}^{pq} + \frac{1}{2}4\pi N \int_0^\infty u^2 du \mathcal{V}(u) \bar{n}_c^{LDA}(u). \quad (5.65)$$

It will actually prove useful to write this in the equivalent form

$$E = \gamma_p^q h_q^p + \Gamma_{pq}^{rs} g_{rs}^{pq} - \Xi_{pq}^{rs} \mathcal{V}_{rs}^{pq} + \int d\mathbf{r} n(\mathbf{r}) \int_0^\infty \frac{1}{2}4\pi u^2 du \mathcal{V}(u) n_c^{LDA}[n(\mathbf{r}); u]. \quad (5.66)$$

In the last term, we may carry out the integral over u to obtain an energy density $\epsilon(\mathbf{r})$, so that the total energy is

$$E = \gamma_p^q h_q^p + \Gamma_{pq}^{rs} g_{rs}^{pq} - \Xi_{pq}^{rs} \mathcal{V}_{rs}^{pq} + \int d\mathbf{r} n(\mathbf{r}) \epsilon(\mathbf{r}). \quad (5.67)$$

We can now define matrix elements ϵ_p^q in the usual way, so that the entire energy is written in terms of matrix elements and density matrices, as

$$E = \gamma_p^q (h_q^p + \epsilon_q^p) + \Gamma_{pq}^{rs} (g_{rs}^{pq} - \mathcal{V}_{rs}^{pq}) + \frac{1}{2}\gamma_p^{[r}\gamma_q^{s]} \mathcal{V}_{rs}^{pq}. \quad (5.68)$$

Differentiation of this energy with respect to the one-matrix yields the one-particle part of the Hamiltonian whose expectation value this energy is, while differentiation with respect to the two-matrix yields the two-particle part of that Hamiltonian.

Recalling that $\mathcal{V}(u)$ and $\epsilon(r)$ are functionals of the density, and noting the presence of the product of one-matrices going along with the matrix elements of \mathcal{V} , it is clear that the Hamiltonian of interest will depend on the density matrices. Nevertheless, it can be constructed.

In order to deal with the derivatives of quantities which depend on the density, we use the following relation:

$$\frac{\delta f[n]}{\delta \gamma_p^q} = \int d\mathbf{r} \frac{\delta f[n]}{\delta n(\mathbf{r})} \frac{\delta n(\mathbf{r})}{\delta \gamma_p^q} = \int d\mathbf{r} \frac{\delta f[n]}{\delta n(\mathbf{r})} \varphi_q(\mathbf{r}) \varphi^p(\mathbf{r}). \quad (5.69)$$

Thus, the derivative of some quantity $f[n]$ with respect to the one-matrix is the matrix element of the derivative of f with respect to n . With this in mind, we have, then

$$H = h_q^p c_p c^q + \frac{1}{4} g_{[rs]}^{pq} c_p c_q c^s c^r + \left(\epsilon_q^p + \gamma_s^r [\bar{\epsilon}_{sq}^{rp} + \mathcal{V}_{sq}^{[rp]}] - \frac{1}{4} \Xi_{rs}^{tu} \bar{\mathcal{V}}_{tuq}^{rsp} \right) c_p c^q - \frac{1}{4} \mathcal{V}_{[rs]}^{pq} c_p c_q c^s c^r. \quad (5.70)$$

Here, we have two new symbols, which are

$$\bar{\epsilon}_{sq}^{rp} = \int \frac{\delta \epsilon_s^r}{\delta n} \varphi_q \varphi^p \quad (5.71)$$

and

$$\bar{\mathcal{V}}_{tuq}^{rsp} = \int \frac{\delta \mathcal{V}_{tu}^{rs}}{\delta n} \varphi_q \varphi^p. \quad (5.72)$$

The first two terms of (5.70) form the usual Hamiltonian H_0 ; the rest is the cusp correction thereto, so that we have

$$H[\Gamma] = H_0 + \delta H_{\text{cusp}}[\Gamma]. \quad (5.73)$$

A somewhat more transparent form, perhaps, is

$$\begin{aligned} H = & (h_q^p + \epsilon_q^p) c_p c^q + \frac{1}{4} (g_{rs}^{[pq]} - V_{rs}^{[pq]}) c_p c_q c^s c^r \\ & + \gamma_r^s (\mathcal{V}_{sq}^{[rp]} + \bar{\epsilon}_{sq}^{rp}) c_p c^q - \Xi_{tu}^{rs} \bar{\mathcal{V}}_{rsq}^{tup} c_p c^q. \end{aligned} \quad (5.74)$$

This separates the terms that depend explicitly on the density from those that do not. It also allows us to note that the two-electron operator in this modified Hamiltonian is no longer simply $g(u) = 1/u$, but is instead $g(u) - \mathcal{V}(u)$. Recalling that $\mathcal{V}(u) = f(u)/u$ and that we have demanded that the cutoff function satisfy $f(u) = 1 + \mathcal{O}(u^2)$, it can be seen that the new electron-electron interaction potential is explicitly nonsingular at $u = 0$, and that the correlation cusp is hence removed from the Hamiltonian.

This, unfortunately, has been accomplished at the price of introducing dependence on the density matrices. Thus, a rigorous approach would require solving for the correlated density matrices, inserting them to redefine the cusp-corrected Hamiltonian, and iterating to self-consistency. The benefit of doing so is that all the standard methods for generating excited states, properties, and so forth would follow without further modification. The cost is that the iterative procedure would be far more time consuming.

Since our goal is to reduce computational expense, in this work we investigate the effect of performing a usual correlated calculation only once, building the changes to the Hamiltonian due to the cusp, and evaluating their effect on the total energy. This corresponds to the first iteration in our iterative scheme, and does not allow the density matrices to adjust to the cusp. It may be the case that using an inexpensive second-order calculation to form the density-matrices and thus the cusp-corrected Hamiltonian to be solved with CC theory would provide a reasonably inexpensive and accurate alternative.

Irrespective of how the cusp-corrected Hamiltonian is to be formed and solved, however, we require some form of exact result against which we can compare

our model for the correlation hole and a standard *ab initio* model for the same quantity. This, in turn, means knowing a correlated wavefunction analytically, but fortunately we are provided with just such a wavefunction in the model system known as Hooke's atom. We will discuss this system at some length in the following chapter, before returning to the assessments of our model in Chapter 7.

CHAPTER 6

HOOKE'S ATOM

Hooke's atom is a system in which two electrons are attached to a center by springs, rather than by the Coulomb interaction (in other words, Hooke's atom is a two-electron harmonic oscillator). There is a long history of investigating this problem, culminating with an explicit solution found by Kais, Herschbach, and Levine in 1989 [86] and a general class of solutions found four years later by Taut [87]. The original Kais solution is in fact the simplest, and we will use it to generate an analytic correlation hole, but we will derive it as a special case of the general solution found by Taut.

6.1 Explicit Solution

The position space representation of the Hooke's atom Hamiltonian is

$$H = -\frac{1}{2m}(\nabla_1^2 + \nabla_2^2) + \frac{1}{2}m\omega^2(r_1^2 + r_2^2) + \frac{1}{r_{12}}. \quad (6.1)$$

It is clear that if we define the usual relative and center-of-mass coordinates

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \quad (6.2a)$$

$$\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), \quad (6.2b)$$

the Hamiltonian is separable, becoming

$$H = -\frac{1}{2}\left(\frac{1}{M}\nabla_R^2 + \frac{1}{\mu}\nabla_r^2\right) + \frac{1}{2}\omega^2(MR^2 + \mu r^2) + \frac{1}{r}, \quad (6.3)$$

where $M = 2m$ is the total mass and $\mu = \frac{1}{2}m$ is the reduced mass. Since we work in atomic units, $m = 1$, hence $M = 2$ and $\mu = \frac{1}{2}$.

The center-of-mass Hamiltonian is just the Hamiltonian for a three-dimensional harmonic oscillator, the ground state energy of which is of course $\frac{3}{2}\omega$ and the (non-normalized) ground state wavefunction of which is

$$\Phi_R = e^{-\frac{1}{2}M\omega R^2}. \quad (6.4)$$

The relative Hamiltonian is something new, containing both a harmonic oscillator potential and a repulsive Coulomb potential. It is, however, spherically symmetric, so that we may write the relative wavefunction as

$$\psi_r = Y_{\ell m}(\hat{r}) \frac{\phi(r)}{r}, \quad (6.5)$$

where $Y_{\ell m}$ is a spherical harmonic and \hat{r} is the direction of r . Note that the symmetry of the wavefunction under interchange of r_1 and r_2 is controlled by the spherical harmonic (R is symmetric under this interchange, as is the norm of r , while \hat{r} changes sign). If the wavefunction is to be symmetric (antisymmetric) under this interchange, $Y_{\ell m}(-\hat{r})$ must equal $Y_{\ell m}(\hat{r})$ ($-Y_{\ell m}(\hat{r})$) and ℓ must hence be even (odd). If, of course, the spatial wavefunction is symmetric under this interchange, the spin part of the wavefunction must be antisymmetric (and hence a singlet), whereas if the spatial wavefunction is antisymmetric, the spin part of the wavefunction must be symmetric and hence a triplet. Therefore, solutions for the relative wavefunction with even ℓ correspond to singlet states, and solutions with odd ℓ correspond to triplet states.

All this being established, our lone remaining task is to solve the radial equation for $\phi(r)$, that equation being

$$-\frac{1}{2\mu} \frac{d^2\phi(r)}{dr^2} + \frac{\ell(\ell+1)}{2\mu r^2} \phi(r) + \frac{1}{2} \mu \omega^2 r^2 \phi(r) + \frac{1}{r} \phi(r) = E_r \phi(r). \quad (6.6)$$

It proves convenient to scale the coordinates as $\bar{r}^2 = \mu\omega r^2$, whereupon (6.6) becomes (dividing by the common factor of ω)

$$-\frac{1}{2} \frac{d^2\phi(\bar{r})}{d\bar{r}^2} + \frac{\ell(\ell+1)}{2\bar{r}^2}\phi(\bar{r}) + \frac{1}{2}\bar{r}^2\phi''(\bar{r}) + \frac{\sigma}{\bar{r}}\phi'(\bar{r}) = \epsilon\phi(\bar{r}), \quad (6.7)$$

with $\sigma^2 = \frac{\mu}{\omega}$ and $\epsilon = \frac{E}{\omega}$.

To solve this equation, we explicitly separate the long-range and short-range behaviors of $\phi(\bar{r})$, writing

$$\phi(\bar{r}) = e^{-\frac{1}{2}\bar{r}^2} \bar{r}^{\ell+1} f(\bar{r}), \quad (6.8)$$

where $f(\bar{r})$ is expanded in power series as

$$f(\bar{r}) = \sum_{k=0}^{\infty} c_k \bar{r}^k. \quad (6.9)$$

Taking $c_0 = 1$ without loss of generality, we obtain

$$c_1 = \frac{\sigma}{\ell+1}, \quad (6.10)$$

in agreement with general cusp condition of (2.4). The remaining coefficients are determined by the three-term recursion relation

$$kc_k = \frac{2\sigma}{2\ell+k+1} c_{k-1} + \frac{2k+2\ell-2\epsilon-1}{2\ell+k+1} c_{k-2}. \quad (6.11)$$

Let us now assume that the series expansion of $f(\bar{r})$ terminates at $k = n - 1$, so that $c_k = 0 \forall k \geq n$. This requires $c_n = 0$ and $c_{n+1} = 0$. Assuming $c_n = 0$ for the moment, the recursion relation (6.11) for $k = n + 1$ becomes

$$(n+1)c_{n+1} = \frac{2n+2\ell-2\epsilon+1}{2\ell+n+2} c_{n-1}. \quad (6.12)$$

That c_{n+1} vanishes requires

$$\epsilon = \ell + n + \frac{1}{2}. \quad (6.13)$$

With this value for ϵ , we now have c_n as a function of σ alone, and must solve for the value of σ which makes c_n vanish.

To carry out this procedure, then, one merely chooses quantum numbers ℓ and n for the relative harmonic oscillator, obtains an energy given by

$$E_r = (\ell + n + \frac{1}{2})\omega, \quad (6.14)$$

and finds the particular frequency ω for which the above energy is an eigenvalue of the relative Hamiltonian. Taut's procedure provides one solution for each of a discrete set of frequencies, and does not guarantee that the solution found corresponds to the ground state.

The original solution of Kais, Herschbach, and Levine corresponds to $n = 2$ and $\ell = 0$, so that the relative energy is $E_r = \frac{5}{2}\omega$. The recursion relation gives us

$$2c_2 = \frac{2}{3}\sigma^2 - \frac{2}{3}, \quad (6.15)$$

where we have used the result (6.10) for $\ell = 0$ to obtain $c_1 = \sigma$. Clearly, this solution holds only for $\sigma = 1$, in which case $\omega = \mu = \frac{1}{2}$. The Kais solution, then, is for $\omega = \frac{1}{2}$, has total energy $E = 2$, and has spatial wavefunction

$$\Psi(R, r) = \frac{1}{2\pi\sqrt{5\pi + 8\sqrt{\pi}}} e^{-\frac{1}{2}R^2 - \frac{1}{8}r^2} \left(1 + \frac{1}{2}r\right). \quad (6.16)$$

Note that were the electrons non-interacting, the ground state wavefunction for the same frequency would be

$$\Psi(R, r) = e^{-\frac{1}{2}R^2 - \frac{1}{8}r^2}, \quad (6.17)$$

so that the Kais solution is simply the wavefunction for non-interacting electrons multiplied by a factor to include the correlation cusp.

While we will not use the wavefunction in this work, the exact solution with $\ell = 0$ and $n = 3$ is found at $\omega = \frac{1}{10}$, and has total energy $E = \frac{1}{2}E_H$.

6.2 Approximations for the Ground-State Energy

Although for select frequencies we can obtain the exact ground state energy, we will wish to have essentially exact energies independent of basis set, and which

require no extrapolation. These highly accurate results would allow us to test our own model against basis set independent benchmarks. In order to find these results, we will use two techniques: perturbation theory, and straightforward application of the variational principle.

6.2.1 Perturbative Estimate of the Ground-State Energy

If we assume that the frequency in which we are interested is large, we can treat the electron repulsion part of the Hamiltonian as a perturbation. Thus, our Hamiltonian is

$$H^{(0)} = -\frac{1}{2\mu} \nabla^2 + \frac{1}{2}\mu\omega^2 r^2 \quad (6.18a)$$

$$H^{(1)} = \frac{1}{r} \quad (6.18b)$$

Because the ground state of the system has $\ell = 0$ and the perturbation is likewise spherically symmetric, the only states which mix with the ground state also have $\ell = 0$.

The $\ell = 0$ states of $H^{(0)}$ can be written as

$$\Psi_n^{(0)}(r) = B_n \frac{1}{r} H_{2n+1}(\sqrt{\mu\omega}r) e^{-\frac{1}{2}\mu\omega r^2}, \quad (6.19)$$

where B_n is just the normalization constant. These states have associated energies $E_n = (2n + \frac{3}{2})\omega$, and n can be any nonnegative integer.

The normalization integral is

$$\int_0^\infty dr e^{-\mu\omega r^2} H_{2n+1}(\sqrt{\mu\omega}r)^2 = 4^n (2n+1)! \sqrt{\frac{\pi}{\mu\omega}}, \quad (6.20)$$

so that the normalization constant becomes

$$B_n = \frac{(-1)^n}{2^n \sqrt{(2n+1)!}} \left(\frac{\mu\omega}{\pi}\right)^{\frac{1}{4}}, \quad (6.21)$$

where the overall phase of the wavefunction was chosen for later convenience.

For the first few orders of the energy, we need only matrix elements between the ground state and the n^{th} excited state. That is, we need

$$V_0^n = B_0 B_n \int_0^\infty \frac{dr}{r} e^{-\mu\omega r^2} H_1(\sqrt{\mu\omega}r) H_{2n+1}(\sqrt{\mu\omega}r). \quad (6.22)$$

We define $x = \sqrt{\mu\omega}r$ and note that $H_1(x) = 2x$, so that we have

$$V_0^n = 2B_0 B_n \int_0^\infty dx e^{-x^2} H_{2n+1}(x), \quad (6.23)$$

Using (C.2), we can write this as

$$V_0^n = 2B_0 B_n \int_0^\infty dx (-1)^{2n+1} \frac{d^{2n}}{dx^{2n}} \frac{d}{dx} e^{-x^2} \quad (6.24a)$$

$$= 2B_0 B_n (-1)^{2n+1} \frac{d^{2n}}{dx^{2n}} e^{-x^2} \Big|_0^\infty \quad (6.24b)$$

$$= -2B_0 B_n e^{-x^2} H_{2n}(x) \Big|_0^\infty \quad (6.24c)$$

$$= 2B_0 B_n H_{2n}(0) \quad (6.24d)$$

$$= 2B_0 B_n (-2)^n (2n-1)!! \quad (6.24e)$$

Inserting the definition of the normalization constants, we find

$$V_0^n = 2 \sqrt{\frac{\mu\omega}{\pi}} \frac{(2n-1)!!}{\sqrt{(2n+1)!}}. \quad (6.25)$$

The energy through first order, then, is

$$E_{[1]} = E^{(0)} + E^{(1)} = E^{(0)} + V_0^0 = \frac{3}{2}\omega + 2 \left(\frac{\mu\omega}{\pi} \right)^{\frac{1}{2}}. \quad (6.26)$$

The second-order energy is

$$E^{(2)} = \sum_{n=1}^{\infty} \frac{V_0^n V_n^0}{E_0^{(0)} - E_n^{(0)}} \quad (6.27a)$$

$$= -\frac{2\mu}{\pi} \sum_{n=1}^{\infty} \binom{2n}{n} \frac{(2n)!}{(2n+1)! 4^n n} \quad (6.27b)$$

$$= -\frac{2\mu}{\pi} \sum_{n=1}^{\infty} \binom{2n}{n} \frac{1}{(2n+1) 4^n n} \quad (6.27c)$$

$$= -\frac{\mu}{3\pi} {}_4F_3(1, 1, \frac{3}{2}, \frac{3}{2}; 2, 2, \frac{5}{2}; 1). \quad (6.27d)$$

Here, ${}_4F_3$ is a hypergeometric function, but alas the expression cannot be simplified further and must be evaluated numerically, which results in

$$E_{[2]} \approx \frac{3}{2}\omega + 2\sqrt{\frac{\mu\omega}{\pi}} - 0.15578\mu. \quad (6.28)$$

Estimating the energy beyond second order would require the evaluation of more general matrix elements, but since even the second-order energy is only evaluated numerically, we abandon perturbation theory in favor of a variational estimate of the ground state energy.

6.2.2 Variational Estimate of the Ground-State Energy

The variational wavefunction we will use takes the form

$$\tilde{\psi}(r) = e^{-\frac{1}{4}\omega r^2} (1 + \frac{1}{2}r + ar^2 + br^3) \quad (6.29)$$

where we variationally optimize the parameters a and b as functions of ω . The resulting expressions for the variationally optimal parameters are extremely complicated and offer no insight, and the expression for the variationally optimum energy is of course likewise. We merely use these formulae to obtain ground state energies for Hooke's atom which are substantially more accurate than what one obtains with perturbation theory.

By adding a third variational parameter (adding cr^4 in the polynomial), we are able to check the accuracy of our variational calculations. The effect of this third parameter is to change the energy by a quite small amount; at low frequencies (below about $\omega = 1$), the third parameter changes the energy at the sub-microHartree scale. As the frequency grows, so too does the effect of the third parameter, so that at $\omega = 50$, the change in the energy is $45\mu E_H$, which is still better than the $0.1mE_H$ accuracy we will require.

A final way of estimating the energy which combines the computational ease of the perturbative approach with the accuracy of the variational approach is to use variational calculations and the known large ω result to fit a Padé approximant for the energy. Writing

$$E_P = 3\omega \frac{\sum_{k=0}^4 a_k \omega^{k/2}}{\sum_{k=0}^4 b_k \omega^{k/2}}, \quad (6.30)$$

we force the large ω expansion of E_P to satisfy (6.28), force E_P to be exact for $\omega = \frac{1}{2}$ and $\omega = \frac{1}{10}$, and fit the four remaining coefficients to the three-parameter variational result at $\omega = 1, 2, 3$, and 4 . The resulting coefficients are given in Table 6–1.

Table 6–1: Parameters in the Padé approximant

i	a_i	b_i
0	1	0.103031
1	15.734556	6.173977
2	92.038237	50.964821
3	159.006541	155.661478
4	12.577243	12.577243

For frequencies smaller than $\omega = 30$, the Padé fit agrees with the three-parameter variational result to within one microHartree, except at frequencies below $\omega = 0.1$, where the Padé fit is rather unreliable. This is not cause for concern, since we are not interested in the small ω limit in this work.

6.3 Derivation of the Exchange-Correlation Hole

Because the Kais wavefunction is exact but quite simple, Hooke's atom provides an excellent test system for any model of the exchange-correlation hole we might choose to make. To this end, we construct the system averaged, spherically averaged exchange-correlation hole in Hooke's atom, obtaining this quantity in closed form wherever possible (as we shall shortly see, there are contributions which must be evaluated numerically). Throughout this section, we have sketched the procedure; full details are deferred to Appendix D. In particular, certain integrals appear so often and are straightforward enough that we have just carried them out; these integrals are all evaluated in Appendix D.

We begin by restating the definition of the system averaged, spherically averaged exchange-correlation hole, given in (4.77) as

$$\bar{n}_{xc}(u) = \frac{1}{N} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\delta(r_{12} - u)}{4\pi u^2} [2n_2(\mathbf{r}_1, \mathbf{r}_2) - n(\mathbf{r}_1)n(\mathbf{r}_2)]. \quad (6.31)$$

It proves convenient to define the coordinate $\mathbf{r}_{1u} = \mathbf{r}_2 = \mathbf{r}_1 + \mathbf{u}$, which we will use extensively. One virtue of its use is that it enables us to rewrite the hole in the fairly compact form

$$\bar{n}_{xc}(u) = \frac{1}{4\pi N} \int d\mathbf{r}_1 d\Omega_u [2n_2(\mathbf{r}_1, \mathbf{r}_{1u}) - n(\mathbf{r}_1)n(\mathbf{r}_{1u})]. \quad (6.32)$$

Note the symmetry under interchange of \mathbf{r}_1 and \mathbf{r}_2 in (6.31) is equivalent to symmetry under interchange of \mathbf{r}_1 and \mathbf{r}_{1u} .

The system averaged, spherically averaged exchange-correlation hole splits quite naturally into a contribution from the pair density, which we denote $\bar{n}_2(u)$, minus a contribution from the product of densities, denoted by $\bar{n}_{Coul}(u)$. This latter piece is the Coulomb analogue of the exchange and correlation holes, so that in finding the averaged exchange-correlation hole, what we are doing in effect is solving for the averaged pair density and subtracting the averaged Coulomb hole.

6.3.1 The Averaged Hooke's Atom Pair Density

Examining first $\bar{n}_2(u)$ for our two electron wavefunction and with the normalization constant written for brevity as A , we have

$$\bar{n}_2(u) = \frac{1}{8\pi} A^2 \int d\Omega_u \int d\mathbf{r}_1 e^{-\frac{1}{2}(r_1^2 + r_{1u}^2)} (1 + \frac{1}{2}u)^2. \quad (6.33)$$

The angular integrations result in

$$\bar{n}_2(u) = 2\pi \frac{(1 + \frac{1}{2}u)^2}{u} e^{-\frac{1}{2}u^2} A^2 \int_0^\infty dr r e^{-r^2} \sinh(ur), \quad (6.34)$$

and this last radial integration leaves us with

$$\bar{n}_2(u) = \frac{1}{2} A^2 \pi^{\frac{3}{2}} (1 + \frac{1}{2}u)^2 e^{-\frac{1}{4}u^2}. \quad (6.35)$$

Both the angular and the radial integrations are of the sort which will appear so frequently in the next several pages that we have simply written the results and deferred the evaluation to the appendix.

6.3.2 The Hooke's Atom Density

In order to proceed further, we must evaluate the density for the Hooke's atom wavefunction. This will prove useful later in any event, as we will need it if we are to obtain the LDA correlation hole with the exact density. The density for our wavefunction is

$$n(r_1) = 2A^2 e^{-\frac{1}{2}r_1^2} \int d\mathbf{r}_2 e^{-\frac{1}{2}r^2} (1 + \frac{1}{2}r_{12}). \quad (6.36)$$

Changing the variable of integration to r_{12} gives us

$$n(r_1) = 2A^2 e^{-r_1^2} \int dr e^{-\frac{1}{2}(r^2 - 2rr_1 \cos(\theta))} (1 + \frac{1}{2}r)^2. \quad (6.37)$$

The angular integrations leave us with

$$n(r_1) = \frac{8\pi A^2}{r_1} e^{-r_1^2} \int_0^\infty dr r e^{-\frac{1}{2}r^2} (1 + \frac{1}{2}r)^2 \sinh(rr_1). \quad (6.38)$$

This is another radial integral which can be evaluated in many ways; the resulting density is just

$$n(r) = 8\pi A^2 e^{-\frac{1}{2}r^2} \left[\sqrt{\frac{\pi}{2}} \frac{7+r^2}{4} + e^{-\frac{1}{2}r^2} + \sqrt{\frac{\pi}{2}} \frac{1+r^2}{r} \operatorname{erf}\left(\frac{r}{\sqrt{2}}\right) \right]. \quad (6.39)$$

6.3.3 The Averaged Hooke's Atom Coulomb Hole

Because the Hooke's atom density is rather complicated, we evaluate the Coulomb hole by splitting the density into its constituent pieces. To this end, we write

$$f_1(r) = \sqrt{\frac{\pi}{2}} \frac{7+r^2}{4} \quad (6.40a)$$

$$f_2(r) = e^{-\frac{1}{2}r^2} \quad (6.40b)$$

$$f_3(r) = \sqrt{\frac{\pi}{2}} \frac{1+r^2}{r} \operatorname{erf}\left(\frac{r}{\sqrt{2}}\right) \quad (6.40c)$$

and denote the sum of f_1 , f_2 , and f_3 as f , so that the averaged Coulomb hole becomes

$$\bar{n}_{Coul}(u) = 8\pi A^4 \int d\Omega_u \int d\mathbf{r}_1 e^{-\frac{1}{2}(r_1^2+r_{1u}^2)} f(r_1) f(r_{1u}). \quad (6.41)$$

Defining the intermediate pieces

$$\mathcal{I}_{i,j} = 8\pi A^4 \int d\Omega_u \int d\mathbf{r}_1 e^{-\frac{1}{2}(r_1^2+r_{1u}^2)} f_i(r_1) f_j(r_{1u}), \quad (6.42)$$

we note that $\mathcal{I}_{i,j} = \mathcal{I}_{j,i}$ due to the previously noted symmetry under interchange of \mathbf{r}_1 and \mathbf{r}_{1u} . Thus, the averaged Coulomb hole is simply

$$\bar{n}_{Coul}(u) = \mathcal{I}_{1,1} + \mathcal{I}_{2,2} + \mathcal{I}_{3,3} + 2\mathcal{I}_{1,2} + 2\mathcal{I}_{1,3} + 2\mathcal{I}_{2,3}. \quad (6.43)$$

We will evaluate each piece in turn.

The first piece is

$$\mathcal{I}_{1,1} = \frac{\pi^2}{4} A^4 \int d\Omega_u \int dr_1 e^{-\frac{1}{2}(r_1^2 + r_{1u}^2)} (7 + r_1^2)(7 + r_{1u}^2) \quad (6.44a)$$

$$= \frac{4\pi^4}{u} A^4 e^{-\frac{1}{2}u^2} \int_0^\infty dr r e^{-r^2} (7 + r^2)(9 + r^2 + u^2) \sinh(ur) \quad (6.44b)$$

$$-8\pi^4 A^4 e^{-\frac{1}{2}u^2} \int_0^\infty dr r^2 e^{-r^2} (7 + r^2)(9 + r^2 + u^2) \cosh(ur) \quad (6.44b)$$

$$= \frac{\pi^{\frac{9}{2}}}{16} A^4 e^{-\frac{1}{4}u^2} (1180 + 60u^2 + u^4). \quad (6.44c)$$

The next term we evaluate is

$$2\mathcal{I}_{1,2} = (2\pi)^{\frac{3}{2}} A^4 \int d\Omega_u \int dr_1 e^{-\frac{1}{2}(r_1^2 + r_{1u}^2)} (7 + r_1^2) \quad (6.45a)$$

$$= \frac{2}{u} (2\pi)^{\frac{7}{2}} A^4 e^{-u^2} \int_0^\infty dr r (7 + r^2) \sinh(2ur) e^{-\frac{3}{2}r^2} \quad (6.45b)$$

$$= \frac{128\sqrt{3}}{81} \pi^4 A^4 e^{-\frac{1}{2}u^2} (18 + u^2). \quad (6.45c)$$

We now turn to the contribution from $\mathcal{I}_{1,3}$, which is

$$2\mathcal{I}_{1,3} = 2\pi^2 A^4 \int d\Omega_u \int dr_1 e^{-\frac{1}{2}(r_1^2 + r_{1u}^2)} \frac{1 + r_1^2}{r_1} \operatorname{erf}\left(\frac{r_1}{\sqrt{2}}\right) (7 + r_{1u}^2) \quad (6.46a)$$

$$= \frac{32\pi^4}{u} A^4 e^{-\frac{1}{2}u^2} \int_0^\infty dr (1 + r^2) e^{-r^2} \operatorname{erf}\left(\frac{r}{\sqrt{2}}\right) (9 + r^2 + u^2) \sinh(ur) \\ - 64\pi^4 A^4 e^{-\frac{1}{2}u^2} \int_0^\infty dr (1 + r^2) e^{-r^2} \operatorname{erf}\left(\frac{r}{\sqrt{2}}\right) r \cosh(ur). \quad (6.46b)$$

This radial integral is substantially more difficult to evaluate than what we have seen previously, and we will simplify as far as possible before carrying it out.

First, we write

$$(1 + r^2) e^{-r^2} = \lim_{\alpha \rightarrow 1} \left(1 - \frac{\partial}{\partial \alpha}\right) e^{-\alpha r^2} \equiv \hat{\mathcal{O}} e^{-\alpha r^2}, \quad (6.47)$$

which reduces the number of terms we must carry later. The error function is written in terms of its Fourier transform,

$$\operatorname{erf}(ax) = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{dk}{k} e^{ikx} e^{-\frac{1}{4} \frac{k^2}{a^2}}, \quad (6.48)$$

and at this point the radial integral can be carried out; note that because the rest of the integrand is odd in k and the region is infinite, we may replace $-ie^{ikr}$ with $\sin(kr)$ if we desire. It proves convenient to do so, and to subsequently extend the radial integral to run from $-\infty$ to ∞ . This gives us

$$\begin{aligned} 2\mathcal{I}_{1,3} &= \frac{16\pi^3}{u} A^4 e^{-\frac{1}{2}u^2} \hat{\mathcal{O}} \int_{-\infty}^{\infty} \frac{dk}{k} e^{-\frac{1}{2}k^2} \int_{-\infty}^{\infty} dr (9 + r^2 + u^2) e^{-\alpha r^2} \sin(kr) \sinh(ur) \\ &\quad - 32\pi^3 A^4 e^{-\frac{1}{2}u^2} \int_{-\infty}^{\infty} \frac{dk}{k} e^{-\frac{1}{2}k^2} \int_{-\infty}^{\infty} dr r e^{-\alpha r^2} \sin(kr) \cosh(ur). \end{aligned} \quad (6.49)$$

The radial integrals are evaluated in Appendix D, and after some simplifications, we find

$$\begin{aligned} 2\mathcal{I}_{1,3} &= 8\pi^{\frac{7}{2}} A^4 e^{-\frac{1}{2}u^2} \hat{\mathcal{O}} \frac{1-2\alpha}{\alpha^{\frac{5}{2}}} e^{\frac{1}{4}\frac{u^2}{\alpha}} \int_{-\infty}^{\infty} dk e^{-\frac{1}{2}k^2 - \frac{1}{4}\frac{k^2}{\alpha}} \cos\left(\frac{uk}{2\alpha}\right) \\ &\quad + \frac{4\pi^{\frac{7}{2}}}{u} A^4 e^{-\frac{1}{2}u^2} \hat{\mathcal{O}} \frac{1}{\alpha^{\frac{5}{2}}} e^{\frac{1}{4}\frac{u^2}{\alpha}} \int_{-\infty}^{\infty} \frac{dk}{k} e^{-\frac{1}{2}k^2 - \frac{1}{4}\frac{k^2}{\alpha}} \sin\left(\frac{uk}{2\alpha}\right) P(k), \end{aligned} \quad (6.50)$$

where

$$P(k) = u^2(2\alpha - 1)^2 - k^2 + 2\alpha(1 + 18\alpha). \quad (6.51)$$

The integral over k in the second term we recognize as the Fourier transform of the error function which was just given in (6.48), while the integral in the first term is its derivative with respect to u . Thus, we evaluate everything without much

difficulty, resulting in

$$2\mathcal{I}_{1,3} = -8\pi^4 A^4 \hat{\mathcal{O}} \frac{8\alpha^2 - 1}{\alpha^2(1+2\alpha)^{\frac{3}{2}}} e^{-\frac{\alpha}{1+2\alpha}u^2} + \frac{4\pi^{\frac{9}{2}}}{u} A^4 e^{-\frac{1}{2}u^2} \hat{\mathcal{O}} \frac{u^2(2\alpha-1)^2 + 2\alpha(1+18\alpha)}{\alpha^{\frac{5}{2}}} e^{\frac{1}{4}\frac{u^2}{\alpha}} \operatorname{erf}\left(\frac{u}{2\sqrt{\alpha(1+2\alpha)}}\right). \quad (6.52)$$

The action of the operator $\hat{\mathcal{O}}$ gives the final result,

$$2\mathcal{I}_{1,3} = \frac{2\sqrt{3}}{81} A^4 \pi^4 (1278 + 17u^2) e^{-\frac{1}{3}u^2} + \pi^{\frac{9}{2}} A^4 e^{-\frac{1}{4}u^2} \frac{236 + 36u^2 + u^4}{u} \operatorname{erf}\left(\frac{u}{2\sqrt{3}}\right). \quad (6.53)$$

While $\mathcal{I}_{1,3}$ requires some exertion, $\mathcal{I}_{2,2}$ is simplicity itself, given as it is by

$$\mathcal{I}_{2,2} = 8\pi A^4 \int d\Omega_u \int d\mathbf{r}_1 e^{-(r_1^2 + r_{1u}^2)} \quad (6.54a)$$

$$= \frac{64\pi^3}{u} A^4 e^{-u^2} \int_0^\infty dr r e^{-2r^2} \sinh(2ur) \quad (6.54b)$$

$$= (2\pi)^{\frac{7}{2}} A^4 e^{-\frac{1}{2}u^2}. \quad (6.54c)$$

We now come to

$$2\mathcal{I}_{2,3} = 4(2\pi)^{\frac{3}{2}} A^4 \int d\Omega_u \int d\mathbf{r}_1 e^{-\frac{1}{2}(r_1^2 + 2r_{1u}^2)} \frac{1+r_1^2}{r_1} \operatorname{erf}\left(\frac{r_1}{\sqrt{2}}\right) \quad (6.55a)$$

$$= \frac{8(2\pi)^{\frac{7}{2}}}{u} A^4 e^{-u^2} \int_0^\infty dr e^{-\frac{3}{2}r^2} (1+r^2) \sinh(2ur) \operatorname{erf}\left(\frac{r}{\sqrt{2}}\right). \quad (6.55b)$$

Again, we have a non-trivial radial integration. As before, we Fourier transform the error function and write an operator to simplify the expressions somewhat, this time using

$$\hat{\mathcal{O}} = \lim_{\alpha \rightarrow 1} \left(1 - \frac{2}{3} \frac{\partial}{\partial \alpha}\right) e^{-\frac{3}{2}\alpha r^2} = (1+r^2) e^{-\frac{3}{2}r^2}. \quad (6.56)$$

The result of these manipulations is

$$2\mathcal{I}_{2,3} = \frac{(8\pi)^{\frac{5}{2}}}{2u} A^4 e^{-u^2} \hat{\mathcal{O}} \int_{-\infty}^{\infty} \frac{dk}{k} e^{-\frac{1}{2}k^2} \int_0^{\infty} dr e^{-\frac{3}{2}\alpha r^2} \sin(kr) \sinh(2ur) \quad (6.57a)$$

$$= \frac{64\sqrt{3}\pi^3}{3u} A^4 e^{-u^2} \hat{\mathcal{O}} \alpha^{-\frac{1}{2}} e^{\frac{2}{3}\frac{u^2}{\alpha}} \int_{-\infty}^{\infty} \frac{dk}{k} e^{-\frac{1}{2}k^2 - \frac{1}{6}\frac{k^2}{\alpha}} \sin\left(\frac{2uk}{3\alpha}\right) \quad (6.57b)$$

$$= \frac{64\sqrt{3}\pi^4}{3u} e^{-u^2} \hat{\mathcal{O}} \alpha^{-\frac{1}{2}} e^{\frac{2}{3}\frac{u^2}{\alpha}} \operatorname{erf}\left(\frac{\sqrt{6}u}{3\sqrt{3\alpha^2 + \alpha}}\right) \quad (6.57c)$$

$$= \frac{14(2\pi)^{\frac{7}{2}}}{9} A^4 e^{-\frac{1}{2}u^2} + \frac{256\sqrt{3}\pi^4}{27} A^4 e^{-\frac{1}{3}u^2} \frac{3+u^2}{u} \operatorname{erf}\left(\frac{u}{\sqrt{6}}\right). \quad (6.57d)$$

The radial integration is of the same form as that in $\mathcal{I}_{1,3}$, and we use the result in Appendix D to carry it out.

The last term is by far the most difficult, and must, in fact, be evaluated numerically. We wish, of course, to carry out the integral in closed form as far as possible, reducing the end result to an integral of a finite quantity over a finite range.

We begin with

$$\mathcal{I}_{3,3} = 4\pi^2 A^4 \int d\Omega_u \int dr_1 e^{-\frac{1}{2}(r_1^2 + r_{1u}^2)} \frac{1+r_1^2}{r_1} \operatorname{erf}\left(\frac{r_1}{\sqrt{2}}\right) \frac{1+r_{1u}^2}{r_{1u}} \operatorname{erf}\left(\frac{r_{1u}}{\sqrt{2}}\right). \quad (6.58)$$

Due to the presence of r_{1u} in the error function, the angular integrals are no longer straightforward. One could use a three-dimensional Fourier transformation, but the Fourier integrals become non-trivial instead. Thus, we use a second way of rewriting the error functions, as

$$\frac{\operatorname{erf}\left(\frac{R}{\sqrt{2}}\right)}{R} = \sqrt{\frac{2}{\pi}} \int_0^1 da e^{-\frac{1}{2}a^2 R^2}. \quad (6.59)$$

Writing also an operator

$$\hat{\mathcal{O}} = \lim_{\lambda \rightarrow 1} \lim_{\zeta \rightarrow 1} \left(1 - 2 \frac{\partial}{\partial \lambda}\right) \left(1 - 2 \frac{\partial}{\partial \zeta}\right), \quad (6.60)$$

we arrive at

$$\mathcal{I}_{3,3} = 8\pi A^4 \hat{\mathcal{O}} \int_0^1 da \int_0^1 db \int d\Omega_u \int d\mathbf{r}_1 e^{-\frac{1}{2}\alpha r_1^2} e^{-\frac{1}{2}\beta r_{1u}^2} \quad (6.61a)$$

$$= \frac{128\pi^3}{u} A^4 \hat{\mathcal{O}} \int_0^1 da \int_0^1 \frac{db}{\beta} e^{-\frac{1}{2}\beta u^2} \int_0^\infty dr r e^{-\frac{1}{2}(\alpha+\beta)u^2} \sinh(\beta ur) \quad (6.61b)$$

$$= 8(2\pi)^{\frac{7}{2}} A^4 \hat{\mathcal{O}} \int_0^1 \frac{dadb}{(\alpha+\beta)^{\frac{3}{2}}} e^{-\frac{\alpha\beta}{\alpha+\beta}u^2}. \quad (6.61c)$$

Here, we have, for the sake of brevity, defined

$$\lambda + a^2 = \alpha \quad (6.62a)$$

$$\zeta + b^2 = \beta. \quad (6.62b)$$

Henceforth, unfortunately, things become more complicated rather than less.

Since this integration cannot be performed as written, we will wish to make a change of variables. Before we do so, however, we evaluate the action of the operator; this results in

$$\mathcal{I}_{3,3} = 8(2\pi)^{\frac{7}{2}} A^4 \int_0^1 \frac{dadb}{(\alpha+\beta)^{\frac{7}{2}}} e^{-\frac{1}{2}\frac{\alpha\beta}{\alpha+\beta}u^2} (C_0(\alpha, \beta) + C_1(\alpha, \beta)u^2 + C_2(\alpha, \beta)u^4), \quad (6.63)$$

where the various coefficients in the polynomial in u^2 are

$$C_0(\alpha, \beta) = (\alpha + \beta)^2 + 6(\alpha + \beta) + 15 \quad (6.64a)$$

$$C_1(\alpha, \beta) = \alpha^2 + \beta^2 + 3\frac{\alpha^2 + \beta^2}{\alpha + \beta} - 4\frac{\alpha\beta}{\alpha + \beta} \quad (6.64b)$$

$$C_2(\alpha, \beta) = \left(\frac{\alpha\beta}{\alpha + \beta}\right)^2 \quad (6.64c)$$

and the result of the limits is to set $\alpha = 1 + a^2$ and $\beta = 1 + b^2$.

There are several possible changes of variable which one might try here. None, unfortunately, lead to simple integrals. This being the case, we choose one which leads to a feasible numerical integral. If we envision first using α and β as our

variables of integration, we would have

$$\mathcal{I}_{3,3} = 2(2\pi)^{\frac{7}{2}} A^4 \int_1^2 \frac{d\alpha}{\sqrt{\alpha-1}} \frac{d\beta}{\sqrt{\beta-1}} f(\alpha, \beta), \quad (6.65)$$

with f the integrand in (6.63). Due to the combination $\frac{\alpha\beta}{\alpha+\beta}$ in the exponential, we still are at an impasse. However, we may perform another change of variables, defining $\eta = \frac{\alpha\beta}{\alpha+\beta}$ and integrating with respect to η rather than with respect to β . This yields

$$\mathcal{I}_{3,3} = 2(2\pi)^{\frac{7}{2}} A^4 \int_1^2 \frac{d\alpha}{\alpha^5 \sqrt{\alpha-1}} \int_{\frac{\alpha}{\alpha+1}}^{\frac{2\alpha}{\alpha+2}} \frac{d\eta}{\sqrt{\eta(\alpha+1)-\alpha}} e^{-\frac{1}{2}\eta u^2} (D_0 + D_1 u^2 + D_2 u^4), \quad (6.66)$$

where

$$D_0 = \alpha^4 + 6\alpha^2(\alpha - \eta) + 15(\alpha - \eta)^2 \quad (6.67a)$$

$$D_1 = \alpha^2(2\eta^2 - 2\eta\alpha + \alpha^2) + (\alpha - \eta)(3\alpha^2 - 10\alpha\eta + 10\eta^2) \quad (6.67b)$$

$$D_2 = \eta^2(\alpha - \eta)^2. \quad (6.67c)$$

The integration over η is now possible, using

$$\int \frac{dx}{\sqrt{ax-b}} e^{-\frac{1}{2}u^2x} = \sqrt{\frac{2\pi}{a}} \frac{\operatorname{erf}\left(\sqrt{\frac{ax-b}{2a}}u\right)}{u} e^{-\frac{1}{2}\frac{b}{a}u^2}, \quad (6.68)$$

which follows from the basic integral defining the error function,

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int dx e^{-x^2} = \frac{1}{\sqrt{\pi}} \int \frac{dy}{\sqrt{y}} e^{-y} = \operatorname{erf}(\sqrt{y}). \quad (6.69)$$

Simplifying the resulting rather complicated expression, we arrive at

$$\mathcal{I}_{3,3} = 2(2\pi)^{\frac{7}{2}} A^4 \int_1^2 \frac{d\alpha}{\alpha^5 \sqrt{\alpha-1}} \left(t_1(\alpha, u) \frac{P_1(\alpha, u)}{u} + t_2(\alpha, u) P_2(\alpha, u) \right), \quad (6.70)$$

where

$$t_1(\alpha, u) = \frac{\sqrt{2\pi}\alpha^3}{(\alpha+1)^{\frac{9}{2}}} e^{-\frac{1}{2}\frac{\alpha}{\alpha+1}u^2} \operatorname{erf}\left(\frac{\alpha u}{\sqrt{2(\alpha+1)(\alpha+2)}}\right) \quad (6.71a)$$

$$P_1(\alpha, u) = \alpha^3 u^4 + \alpha(\alpha+1)(\alpha^3 + 4\alpha^2 - \alpha + 2)u^2 \quad (6.71b)$$

$$t_2(\alpha, u) = \frac{2}{(\alpha+2)^{\frac{7}{2}}} e^{-\frac{\alpha}{\alpha+2}u^2} \left(\frac{\alpha}{\alpha+1}\right)^4 \quad (6.71c)$$

$$P_2(\alpha, u) = \alpha(2-\alpha^2)(3\alpha^2+8\alpha+6)u^2 \quad (6.71d)$$

$$+(\alpha+1)(\alpha+2)(2\alpha^4+16\alpha^3+28\alpha^2+3\alpha-16).$$

We are now in a position to evaluate $\mathcal{I}_{3,3}$ as a simple numerical integral. Our only concern is the presence of $\sqrt{\alpha-1}$ in the denominator, which diverges weakly at the lower limit of integration. This divergence, fortunately, can be handled by a variety of techniques; we could eliminate it by partial integration, but as the resulting equations are quite lengthy, we will not bother writing them down and content ourselves with using a numerical integration.

Consolidating the results of (6.44c), (6.45c), (6.53), (6.54c), (6.57d), and (6.70), the system averaged, spherically averaged Coulomb hole is

$$\begin{aligned} \bar{n}_{Coul}(u) &= \frac{\pi^{\frac{9}{2}}}{16} A^4 e^{-\frac{1}{4}u^2} (1180 + 60u^2 + u^4) + \frac{23(2\pi)^{\frac{7}{2}}}{9} A^4 e^{-\frac{1}{2}u^2} \\ &+ 2\sqrt{3}\pi^4 A^4 e^{-\frac{1}{3}u^2} (30 + u^2) + \pi^{\frac{9}{2}} A^4 e^{-\frac{1}{4}u^2} \frac{236 + 36u^2 + u^4}{u} \operatorname{erf}\left(\frac{u}{\sqrt{12}}\right) \\ &+ \frac{256\sqrt{3}}{27} \pi^4 A^4 e^{-\frac{1}{3}u^2} \frac{3 + u^2}{u} \operatorname{erf}\left(\frac{u}{\sqrt{6}}\right) \\ &+ 2(2\pi)^{\frac{7}{2}} A^4 \int_1^2 \frac{d\alpha}{\alpha^5 \sqrt{\alpha-1}} \left(t_1(\alpha, u) \frac{P_1(\alpha, u)}{u} + t_2(\alpha, u) P_2(\alpha, u) \right). \end{aligned} \quad (6.72)$$

Recall that the normalization constant A is

$$A = \frac{1}{2\pi\sqrt{5\pi + 8\sqrt{\pi}}}. \quad (6.73)$$

Finally, recall that with the averaged Coulomb hole of (6.72) and the averaged pair density of (6.35), we can construct the averaged exchange-correlation hole by

$$\bar{n}_{xc}(u) = 2\bar{n}_2(u) - \bar{n}_{Coul}(u). \quad (6.74)$$

It is to this quantity that we will first compare the results of our model, in the ensuing chapter.

6.4 Commentary on the Exchange-Correlation Hole

Before we make detailed comparisons between our exact result and the results from our model and standard *ab initio* calculations, there are a few things which we should discuss briefly.

First, we have not built the exact exchange hole. The reason for this is that constructing the exact one-matrix for the Hooke's atom wavefunction cannot be done in closed form. That is, using the definition of the one-matrix (and not worrying about spin for the moment), we would have

$$n_1(\mathbf{r}_1, \mathbf{r}_2) = 2A^2 e^{-\frac{1}{2}(r_1^2 + r_2^2)} \int d\mathbf{r}_3 e^{-\frac{1}{2}r_3^2} \left(1 + \frac{1}{2}r_{13} + \frac{1}{2}r_{23} + \frac{1}{4}r_{13}r_{23} \right). \quad (6.75)$$

While almost all of these integrals can be carried out without much effort, the term which contains the product $r_{13}r_{23}$ cannot be integrated at all, due to the complicated angular structure. At best, the exact averaged exchange hole can be reduced to terms which include two-dimensional numerical integrations, and since these integrations are quite slow and the exact result, as we shall see in the following chapter, is not really necessary, we have omitted it here.

We can, however, make some progress towards the short-range parts of the Coulomb, exchange, and correlation holes, and we will conclude this chapter by doing so.

First, note that at $u = 0$, we can obtain the exchange hole from the Coulomb hole; this is because the averaged exchange hole is given by

$$\bar{n}_x(u) = -\frac{1}{2} \frac{1}{4\pi N} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\delta(r_{12} - u)}{u} n_1(\mathbf{r}_1, \mathbf{r}_2) n_1(\mathbf{r}_2, \mathbf{r}_1), \quad (6.76)$$

where the spin integrations are assumed to have been carried out. The Coulomb hole, meanwhile, is

$$\bar{n}_{Coul}(u) = \frac{1}{4\pi N} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\delta(r_{12} - u)}{u} n(\mathbf{r}_1) n(\mathbf{r}_2), \quad (6.77)$$

the spin integrations again having been carried out. At $u = 0$, $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{R}_{CM}$, and the product of one-matrices in the exchange hole becomes $n_1(\mathbf{R}_{CM}, \mathbf{R}_{CM})^2$. Thus, the on-top exchange hole requires only the diagonal part of the spin-averaged one-matrix, and we can obtain this from the density. The overall effect is to give us

$$\bar{n}_x(u = 0) = -\frac{1}{2} \bar{n}_{Coul}(u = 0). \quad (6.78)$$

The averaged pair density is, through $\mathcal{O}(u)$,

$$\bar{n}_2(u) = \frac{1}{2} A^2 \pi^{\frac{3}{2}} (1 + u) + \mathcal{O}(u^2). \quad (6.79)$$

The Coulomb hole, meanwhile, ignoring the contribution from $\mathcal{I}_{3,3}$, is

$$\bar{n}_{Coul}(u) = \frac{295}{4} A^4 \pi^{\frac{9}{2}} + \frac{416}{\sqrt{3}} A^4 \pi^4 + \frac{440}{9} \sqrt{2} A^4 \pi^{\frac{7}{2}} + \mathcal{I}_{3,3}(u = 0) + \mathcal{O}(u^2), \quad (6.80)$$

and of course the exchange hole is given by (6.78). Our sole remaining task, therefore, is to evaluate $\mathcal{I}_{3,3}$ at $u = 0$. This is unenlightening at best, so we merely quote the result, that

$$\mathcal{I}_{3,3}(u = 0) = 4(2\pi)^{\frac{7}{2}} A^4 \left(\frac{53}{36} - \frac{11}{8} \sqrt{2} \arctan \left(\frac{7\sqrt{2}}{8} \right) + \frac{11\sqrt{2}}{16} \pi \right). \quad (6.81)$$

Evaluating everything, we have

$$\bar{n}_{Coul}(u) = 0.033671 + \mathcal{O}(u^2) \quad (6.82a)$$

$$\bar{n}_x(u) = -0.016836 + \mathcal{O}(u^2) \quad (6.82b)$$

$$\bar{n}_c(u) = -0.012116 + 0.004719u + \mathcal{O}(u^2) \quad (6.82c)$$

$$\bar{n}_2(u) = 0.0023596 + 0.0023596u + \mathcal{O}(u^2). \quad (6.82d)$$

Note that the on-top pair density is an order of magnitude smaller than any of its constituent pieces; this emphasizes that the factorization of the pair density into Coulomb, exchange, and correlation is of limited utility at short range.

CHAPTER 7

RESULTS OF THE PROPOSED MODEL

We are now in a position to validate the model we have proposed previously, as we have an exact result against which to compare. In this chapter, we will make this comparison, then turn to other systems for which we do not have the exact correlation hole and check the quality of the model there. Throughout this chapter, we will have plots of various exchange and correlation holes; the axes are labeled in atomic units, so that the abscissa is the interelectronic distance in Bohr radii, and the ordinate is the appropriate hole in Hartree per Bohr radius cubed.

7.1 Hooke's Atom, $\omega = \frac{1}{2}$

The analytic exchange-correlation hole for Hooke's atom at $\omega = \frac{1}{2}$ having been constructed, we perform standard *ab initio* calculations and build the exchange-correlation hole from them, as well as from the LDA. The *ab initio* wavefunction we use is the Full CI, a result obtained by diagonalizing the Hamiltonian in the space of antisymmetrized products of one electron functions; apart from the error in using only a finite basis set, this procedure is clearly exact.

The basis sets we use in constructing our wavefunction are Gaussian, with exponents given by 2.7ω , 1.8ω , 1.2ω , 0.7ω , 0.5ω , 0.25ω , and 0.125ω . For angular structure, we use the spherical harmonics with $\ell = 0$ alone (the “*s*-complete” basis set) or with $\ell = 0$ and $\ell = 1$ (the “*sp*-complete” basis set). As we have seven radial functions, the one-particle basis sets have 7 and 28 functions, respectively, so that we have respectively 21 and 406 antisymmetrized products.

These functions seem to be sufficient to cover the relevant portions of space, since additional functions of the appropriate angular momentum have negligible effects on the total energy. As can be seen in Table 7-1, the *s*- and *sp*-basis

sets yield energies of, respectively, 2.0343 E_H and 2.0026 E_H . Adding Cartesian d -functions reduces the error to 0.7 mE_H , while Cartesian f -functions reduce the error to 0.2 mE_H .

Table 7–1: Energies in our test systems

System	E_s	E_{sp}	E_{spd}	\bar{E}_s	\bar{E}_{sp}	E_{CBS}
$Z = 2$	-2.87825	-2.89978	-2.90240	-2.8843	-2.9015	-2.9037
$Z = 3$	-7.25246	-7.27585	-7.27861	-7.2613	-7.2794	-7.2798
$\omega = 0.1$	0.52548	0.50046	0.50013	0.5237	0.5001	0.5000
$\omega = 0.5$	2.03434	2.00263	2.00074	2.0302	2.0007	2.0000
$\omega = 1$	3.76722	3.73385	3.73121	3.7616	3.7310	3.7301
$\omega = 2$	7.09711	7.06260	7.05931	7.0897	7.0585	7.0579
$\omega = 2.5$	8.73014	8.69534	8.69187	8.7220	8.6908	8.6903
$\omega = 3$	10.35044	10.31543	10.31181	10.3417	10.3105	10.3102
$\omega = 3.3$	11.31783	11.28273	11.27904	11.3088	11.2776	11.2774
$\omega = 4$	13.56406	13.52877	13.52494	13.5544	13.5233	13.5232
$\omega = 4.5$	15.16080	15.12540	15.12150	15.1507	15.1197	15.1197
$\omega = 5$	16.75231	16.71681	16.71285	16.7418	16.7108	16.7111
Error	-0.0346	-0.0042	-0.0014	-0.0286	-0.0005	

In Figure 7–1, we show the exchange-correlation holes built from the exact wavefunction, the wavefunctions with s - and sp -functions, and the LDA. Note that the exchange-correlation hole in the sp -basis set is all but exact for $u \gtrsim 2$, while without the presence of p -functions to provide angular correlation, the hole is very poorly described by our basis set. This is a well-known phenomenon: without the presence of functions to add angular structure beyond what the reference determinant contains, the results of correlated and uncorrelated calculations do not differ substantially.

The LDA exchange-correlation hole is remarkably accurate, although it decays much too slowly. This is not easy to see on the scale of the chart, but the LDA crosses under the exact result at approximately $u = 4.25$. However, the LDA hole is superior to the wavefunction hole at short-range and behaves linearly for small u ,

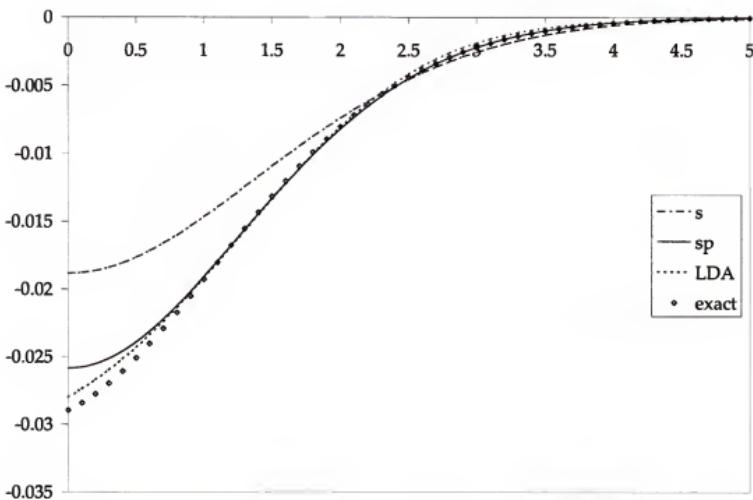


Figure 7-1: Exchange-correlation hole in Hooke's atom, $\omega = \frac{1}{2}$

in agreement with the exact hole and in contrast to either of the holes calculated in our basis set.

We may look a little deeper and consider the exchange and correlation parts separately. While the exact exchange hole is intractable, note from Figure 7-2 that the exchange hole is affected only to a small extent by the inclusion of p -functions, and that the short-range part is essentially identical whether we use s -functions alone, both s - and p -functions, or the LDA. The correlation hole, therefore, is where the distinction between LDA and wavefunction approaches should be manifest, and as can be seen in Figure 7-3, this is indeed the case

All of this is exactly as we expect, and provides us with initial support for two main conclusions: that we can focus solely on the correlation hole (which is sensible, as the exact exchange hole is quadratic for small u , and can hence

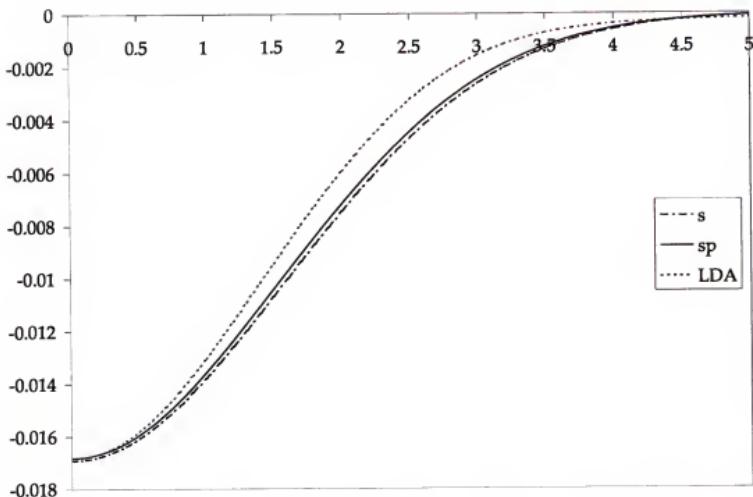


Figure 7-2: Exchange hole in Hooke's atom, $\omega = \frac{1}{2}$

be described in our basis set), and that we may attempt to use the LDA for an improved (but still imperfect) short range description.

This being established, we now turn to assess our model, which requires us to pick a value for the parameter α . Two possibilities for determining this quantity are investigated: demanding that the resulting energy be exact, and demanding that our correction to the correlation hole not change particle number (really, that it integrate to some number smaller than 0.001 in magnitude). We find, respectively, $\alpha = 1.68$ and $\alpha = 2.30$. With the former value for α , the energy is exact by construction but the sum rule is violated to the extent of 0.0017, while with the latter, the sum rule is obeyed to within the desired 0.001 and the error in the total energy is reduced by a factor of 4, from $2.6 mE_H$ to $0.7 mE_H$. Our correlation hole of (5.1), with $\alpha = 2.30$, is shown in Figure 7-3.

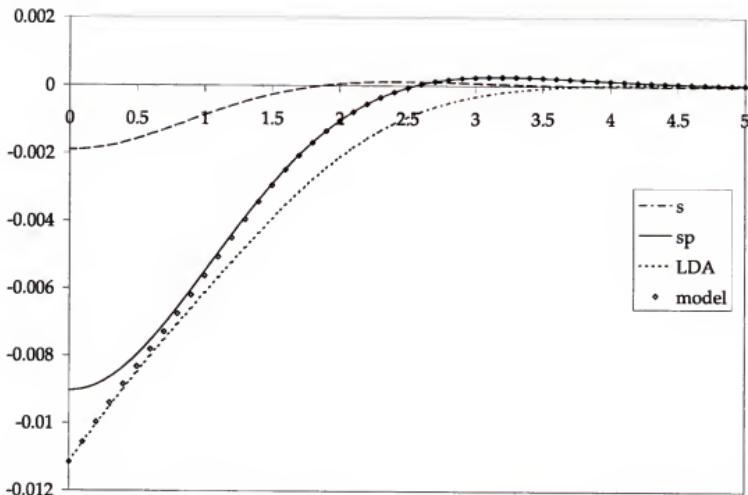


Figure 7-3: Correlation hole in Hooke's atom, $\omega = \frac{1}{2}$

7.2 Hooke's Atom at Other Frequencies

Based upon these results, we have chosen to investigate Hooke's atom at several other frequencies, ranging as low as $\omega = \frac{1}{10}$ and as high as $\omega = 5$. With this range of frequencies, we have systems where the correlation energy is a substantial fraction of the electron interaction energy (which occurs at small frequencies) and where the correlation energy is a small contribution to the electron interaction energy, at large frequencies. The situation usual in quantum chemistry corresponds to ω closer to $\frac{1}{2}$ or 1 than to $\frac{1}{10}$ or 5.

The numerical results are given in Table 7-1, where \tilde{E}_s and \tilde{E}_{sp} come from our model for the correlation hole with α chosen by the criterion that the correlation sum rule is satisfied to one part per thousand. In Table 7-2, we list the corresponding values of α as α_N , and also the values required to yield exact energies, denoted α_E . Note that we have complete basis estimates for the energy in all these cases;

these are based upon the variational estimate of Chapter 5 in the case of Hooke's atom, and by basis set extrapolation for the Coulombic systems.

Table 7–2: Cutoff parameters α in our test systems

System	$\alpha_{N,s}$	$\alpha_{E,s}$	$\alpha_{N,sp}$	$\alpha_{E,sp}$
$Z = 2$	24.2	4.57	6.96	4.79
$Z = 3$	51.5	13.9	18.3	17.5
$\omega = 0.1$	2.46	0.135	0.266	0.237
$\omega = 0.5$	12.2	1.06	2.30	1.68
$\omega = 1$	22.1	2.41	5.06	3.89
$\omega = 2$	38.3	5.33	10.2	8.72
$\omega = 2.5$	45.5	6.84	12.5	11.2
$\omega = 3$	51.8	8.38	14.8	13.8
$\omega = 3.3$	55.6	9.31	16.1	15.3
$\omega = 4$	64.0	11.5	19.0	18.6
$\omega = 4.5$	70.0	13.0	21.1	21.3
$\omega = 5$	75.0	14.7	23.0	24.4

The majority of these calculations show the same features observed in our initial work on Hooke's atom. That is, the exchange holes from LDA and within our basis sets agree at short range, but the LDA falls off too rapidly initially and decays too slowly at long range. The correlation hole from LDA is deeper than that within our basis set at small u (and, of course, linear by construction) and likewise falls off too slowly. Because these features are general, we limit our discussion to Hooke's atom at the highest and lowest frequencies examined.

Let us begin with Hooke's atom at $\omega = 5$. The total energy, from Table 7–1, is $16.7111E_H$, while the exchange energy is $-3.4452E_H$ and the correlation energy is only some $86mE_H$. Correlation thus accounts for about 0.5% of the total energy, and the correlation energy is about 40 times smaller than the exchange energy. This is to be contrasted to the situation with $\omega = \frac{1}{2}$, where the correlation energy is about the same size, but the total energy is an order of magnitude smaller: correlation accounts for 5% of the total energy and is only 10 times smaller than the exchange energy, more typical of chemical systems.

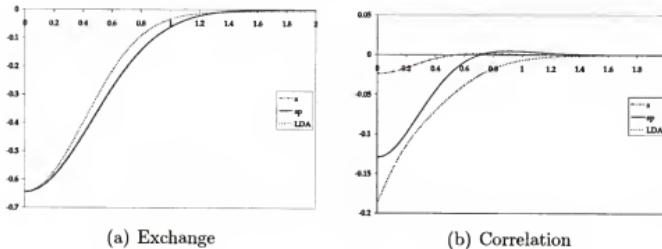


Figure 7-4: Exchange and correlation holes in Hooke's atom, $\omega = 5$

In Figures 7-4a and 7-4b, we see respectively the exchange and correlation holes for this system. Note that the exchange holes within our two basis sets are indistinguishable. As before, the LDA correlation hole is deeper at small u but is inadequate for large u ; the basis set holes agree for sufficiently large u but the hole using only s -functions is far too shallow.

The correlation holes, however, are shorter in range than what is seen with the lower frequency, which is to be expected as the frequency defines a natural length scale $l_0 = 1/\sqrt{\omega}$, so that higher frequencies imply shorter lengths. Also of note is that the LDA corrects the short-range behavior substantially more than in the lower frequency systems. The result of this larger short-range correction is that our model yields a total energy that is better than what we find when we add d -functions to our basis set (a common result) and is actually slightly too negative; here the model overcompensates for the poor short-range correlation description in our usual *ab initio* approach. Note, finally, that the exchange hole is some four or five times deeper than the correlation hole, unlike in the case with $\omega = \frac{1}{2}$, where the exchange is only about 50% deeper than the correlation.

Turning to the other extreme, we use Hooke's atom with $\omega = \frac{1}{10}$ as an example of a strongly correlated system. This is another system where the exact wavefunction can be written, but we have not examined it. The total energy, recall,

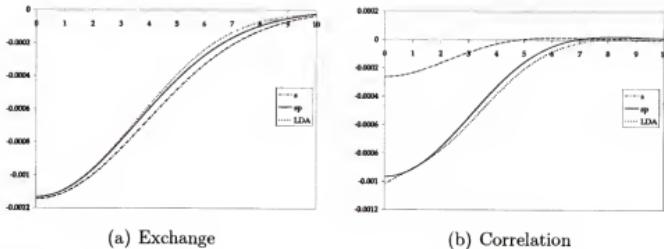


Figure 7-5: Exchange and correlation holes in Hooke's atom, $\omega = \frac{1}{10}$

is exactly $E = \frac{1}{2}E_H$. The correlation energy is still nearly the same size as it was with $\omega = 5$ and accounts, then, for more than 15% of the total energy, obviously a significant component. It is now only six times smaller than the exchange energy; clearly, correlation is substantially more important for this system than in Hooke's atom with a larger frequency.

The exchange holes within our two basis sets, as seen in Figure 7-5a, now differ significantly, which is not unexpected; recall that we use the correlated one-particle density matrix to define the exchange hole, and if correlation is important enough to have a substantial effect on the one-matrix, it is not surprising that higher angular momentum functions, which contribute only through correlation, will modify the exchange hole to a larger extent than normal. (It is for the opposite reason, of course, that the exchange holes at $\omega = 5$ were unaffected by the addition of p -functions.)

The correlation hole, in Figure 7-5b is much longer in range here, but note that the LDA deepens the short-range part only slightly. It thus provides only a small correction, but the result we get by adding d -functions is of about the same accuracy. This is simply due to the small size of the corrections involved, however, rather than any expectation that the model allows us to treat strong correlations simply and accurately. Unlike the case with the larger frequencies, the LDA hole

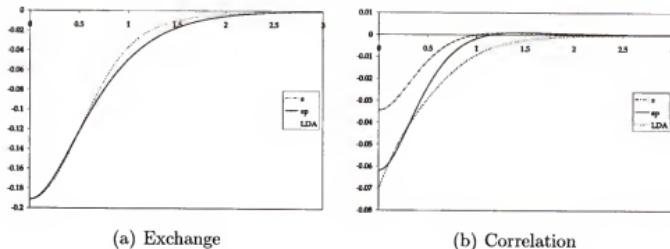


Figure 7-6: Exchange and correlation holes in helium

crosses the sp - hole a few times at short range, which allows the LDA to describe the system reasonably well for somewhat larger distances. One last thing to note about the correlation hole is that it is of comparable depth to the exchange hole, further evidence that the system is strongly correlated.

7.3 Coulombic Systems: Helium, Lithium Cation, and Hydride

Having extracted the relevant data from the assorted specimens of Hooke's atom, we move to Coulombic systems, starting with the helium atom in Figure 7-6. The general features are unchanged. The exchange hole is well described in either basis set, and is in fact essentially unchanged by the addition of p -functions. The LDA exchange hole tracks the basis set hole excellently for smaller values of u before deviating to the positive (and, as always, crossing back under and decaying too slowly).

The LDA correlation hole is, as we have come to expect, deeper than the basis set hole, although not too a great extent. Like the low frequency Hooke's atom, the LDA correlation hole and the hole from the sp -basis set cross twice at short range, so that the LDA works reasonably well over a somewhat longer length scale than one might expect on the basis of Hooke's atom. The effect is to somewhat lessen the correction our model provides; the error is roughly halved, but we do not do as well as we would when adding d -functions. Note that the exchange hole is between

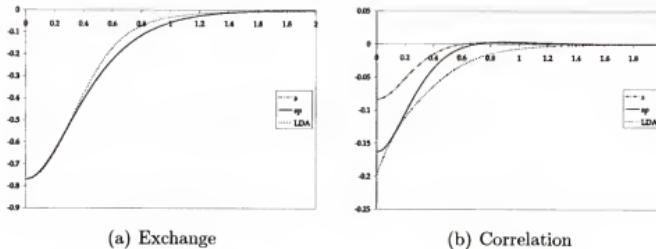


Figure 7-7: Exchange and correlation holes in lithium cation

twice and thrice as deep as the correlation hole, intermediate between Hooke's atoms at $\omega = \frac{1}{2}$ and $\omega = 5$.

The lithium cation, Figure 7-7, follows the same pattern. The exchange is unaffected by adding p -functions, and sits atop the LDA exchange hole at short range. The LDA deepens the correlation somewhat, crossing and recrossing the sp -basis set's hole at short range before becoming unreliable. As is the case with the higher frequency Hooke's atoms, the LDA provides a larger deepening, corresponding to a shorter range of the correlation hole, and leading to an energy from our model superior to that which we get with d -functions involved. As is also the case with the high frequency Hooke's atom, the exchange is four or five times deeper than the correlation.

Finally, we consider hydride, in Figure 7-8. Here, the usual pattern is significantly disrupted. In the case of the exchange hole, the LDA crosses the exact basis set result at substantially larger u than we have hitherto seen, although the basis set result is still largely unaffected by the addition of p -functions, except at short range.

This is not all that unusual, but the situation with correlation is quite different from what we have seen previously; the LDA correlation hole is actually substantially shallower than what we obtain in our sp -complete basis set. Thus, any

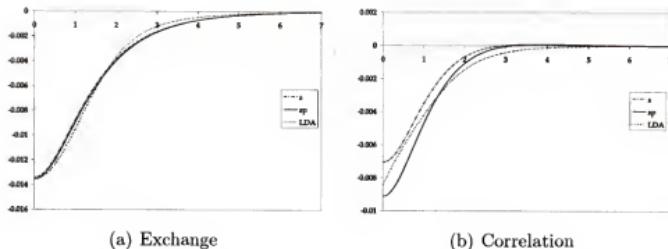


Figure 7-8: Exchange and correlation holes in hydride

correction we might derive at short range is a correction in the wrong direction. It is perhaps noteworthy that the exchange is only 50% deeper than the correlation, not dissimilar to Hooke's atom at $\omega = \frac{1}{2}$; the problem is clearly not that the correlation is too strong for the model to have any success in describing it.

The difficulty with hydride lies not in the strength of the correlation but in the nature of the correlation. For most systems of chemical interest, the correlation which we wish to discuss is angular in nature, as electrons try to stay on opposite sides of an atom. In the case of hydride, there is an unusual amount of radial correlation (this radial correlation, in fact, is largely responsible for the stability of the anion). Thus, one might expect that the reason the model breaks down for hydride is that it fails to properly describe radial correlations, underestimating them substantially.

This is fine as far as it goes, but we have not yet explained why the LDA would fail to describe radial correlations adequately. The reason lies in its inherent locality. Recall from our earlier discussions that the relation between the averaged hole and the pair-correlation function is

$$\bar{n}_{xc}(u) = \frac{1}{N} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\delta(r_{12} - u)}{4\pi u^2} n(\mathbf{r}_1) n(\mathbf{r}_2) g_{xc}(\mathbf{r}_1, \mathbf{r}_2). \quad (7.1)$$

In the LDA, however, we use instead

$$\bar{n}_{xc}^{LDA}(u) = \frac{1}{N} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\delta(r_{12} - u)}{4\pi u^2} n(\mathbf{R})^2 g_{xc}^{LDA}(n(\mathbf{R}, u)). \quad (7.2)$$

Thus, even if the local density approximation for the spherically averaged pair-correlation function is reasonable, the product of densities which multiply it in forming the hole are approximated as well, and in such a way that radial correlations cannot be properly described.

This picture now explains the observation that in systems like the lithium cation, the LDA hole is much deeper relative to the *sp*-basis hole than in systems which are less tightly confined. Strongly confined systems will in general have minimal radial correlations for the LDA to underestimate, so that in these systems the LDA hole should be much deeper than the hole in a basis with only low angular momentum functions, and the model should work very well. In systems such as helium, where the radial correlations are not entirely negligible, the model should work somewhat less well, but so long as angular correlations are dominant our scheme should provide substantial improvement nonetheless. In hydride, the radial correlations are so important and treated so poorly that the model simply fails. In Hooke's atom at low frequencies, this is not the case because the external potential forces the long-range wavefunction to decay more rapidly (as a Gaussian) than in a Coulombic system with its associated exponential decay; this more rapid decay tends to reduce radial correlations somewhat.

In all of these systems, we note that it is possible to get the exact energy using only *s*-functions, at the cost of what we have deemed an unacceptable violation of the sum rule. In addition, the correction is hardly short-range at this point, and one might as well just use the LDA correlation in its entirety. Choosing the cutoff to satisfy the sum rule instead is certainly possible, but then the energy is not improved to any significant degree; hence, it would be vastly preferable to at least

add p -functions, despite the extra cost required, since they provide the majority of the correlation effect. Of course, if we add p -functions and then make use of the proposed correction, adding functions of yet higher angular momentum does not appear to be required.

7.4 Gradient Effects

Having investigated the LDA as a model for short-range correlation, we now examine the effects of gradients. Note that the gradient correction is always positive at short range, and usually fairly small. This is an early indication that gradient effects may not be very important in addressing the short-range correlation, as the model we use for them does not correct the on-top hole at all. In Table 7-3, we show the effects of gradient corrections in all of our test systems, correcting only the correlation holes constructed with the sp -function basis set.

Table 7-3: Effects of gradient corrections in our test systems

System	\bar{E}_{sp}	$\bar{E}_{sp+\nabla}$	E_{CBS}	$\alpha_{N,sp}$	$\alpha_{N,sp+\nabla}$
$Z = 2$	-2.9015	-2.9006	-2.9037	6.96	3.95
$Z = 3$	-7.2795	-7.2789	-7.2798	18.3	12.6
$\omega = 0.1$	0.5001	0.5023	0.5000	0.266	0.0133
$\omega = 0.5$	2.0007	2.0008	2.0000	2.30	1.54
$\omega = 1$	3.7310	3.7310	3.7301	5.06	3.93
$\omega = 2$	7.0585	7.0586	7.0579	10.2	8.35
$\omega = 2.5$	8.6908	8.6908	8.6903	12.5	10.4
$\omega = 3$	10.3105	10.3106	10.3102	14.8	12.3
$\omega = 3.3$	11.2776	11.2777	11.2774	16.1	13.4
$\omega = 4$	13.5233	13.5234	13.5232	19.0	16.0
$\omega = 4.5$	15.1197	15.1197	15.1197	21.1	17.7
$\omega = 5$	16.7108	16.7109	16.7111	23.0	19.4

Note first that the gradient corrections have an all but negligible effect on the total energy in the model, which is quite sensible and shows that the HEG approximation for short range correlation is quite good. Indeed, the gradient corrections are so small compared to the dominant LDA contribution that plots of our model correlation holes with and without gradient corrections are indistinguishable. The

main effects, then, of gradients are to slightly increase the range over which the electron gas portion of the hole extends, that is, gradient corrections lower the value of α without changing the energy in any significant way. Since the inclusion of gradients complicates the analysis somewhat, but fails to improve the results, we will not pursue them further at present; note, however, that we will return to the these results at the end of the next section.

Worth noting, also, is that with gradient effects, the total correction for Hooke's atom with $\omega = \frac{1}{10}$ is positive, not negative. This is due to the combination of two effects. First, the difference between the results from LDA and from our *sp*-basis is small, and secondly, the gradient corrections are inherently positive for small u . They thus correct the small u behavior more than is desired, and the result is that, as in the case with hydride, the model gives unphysically positive corrections for the short-range correlation.

7.5 Models for the Cutoff Length

Now that we have seen several illustrative examples showing the promise of the model, we address the crucial weakness: finding α . We could, of course, build the correlation holes from both the LDA and our correlated wavefunction, and follow the scheme that has been used hitherto, but building the correlation hole is more computationally demanding than it would be to simply add higher angular momentum in our basis set. For reasons both of practicality and elegance, then, we need to find some way of predicting what value α should take, rather than determining it after we have constructed the correlation holes. Fortunately, we have some guidance in doing this, as we know the important characteristic scales of the correlation hole in the HEG.

To begin with, the length scale of the HEG correlation hole is set by the Thomas screening length [82],

$$k_S = \left(\frac{4}{\pi} k_F \right)^{\frac{1}{2}} = 2 \left(\frac{3}{\pi} n \right)^{\frac{1}{6}}. \quad (7.3)$$

We also know that the length scale at which gradient corrections appear is set by [85]

$$t = \frac{\|\nabla n\|}{2n k_S}. \quad (7.4)$$

Thus, the range of our electron gas correction should be formed from some combination of these parameters t and k_S .

We require that the product αu^2 be invariant under a homogeneous scaling $\mathbf{r} \rightarrow \lambda \mathbf{r}$; as u^2 becomes $\lambda^2 u^2$, we evidently have $\alpha \rightarrow \lambda^{-2} \alpha$. Since the density scales as λ^{-3} , both k_S and t scale as $\lambda^{-1/2}$; thus, the parameter α goes like $k_S^p t^q$, where $p + q = 4$.

Because we want α to be a simple number and not a function of the center-of-mass location, we form system-averaged values of the screening length and the gradient length, which we have denoted

$$x = \int d\mathbf{r} \frac{n(\mathbf{r})}{N} t[n(\mathbf{r})]^2 \quad (7.5)$$

and

$$y = \int d\mathbf{r} \frac{n(\mathbf{r})}{N} k_S[n(\mathbf{r})]. \quad (7.6)$$

For the moment, we attempt to write α as some simple power of x or y alone; thus, we must have $\alpha = C_x x^2$ or $\alpha = C_y y^4$.

Let us begin with α as determined to modify the sp -correlation hole. In Figures 7–9 and 7–10, we show α against x^2 and y^4 , respectively. In either case, we show both α_N , determined from the sum rule criterion, and α_E , determined from the energy criterion.

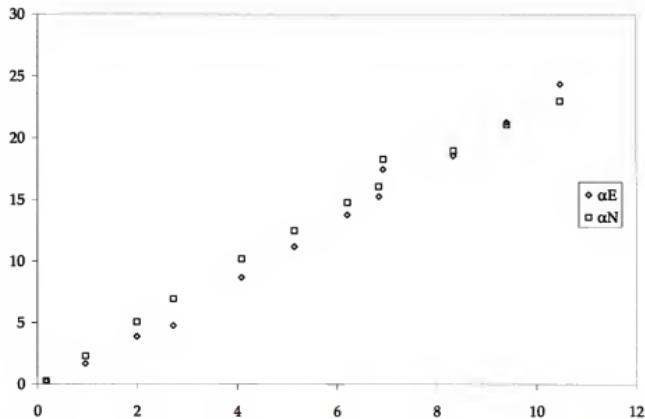


Figure 7-9: Cutoff parameter α from the sp basis set vs. the gradient parameter x^2

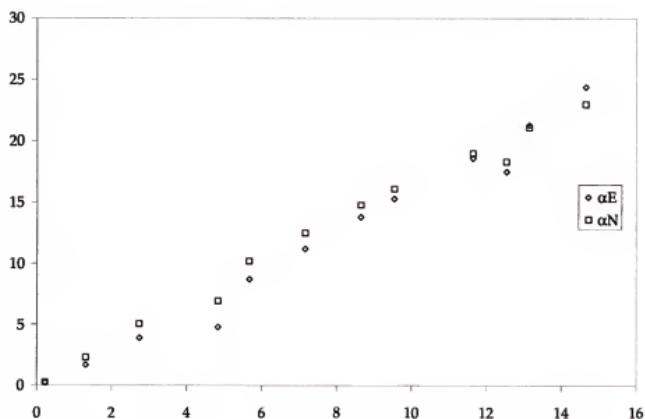


Figure 7-10: Cutoff parameter α from the sp basis set vs. the screening parameter y^4

We first note that writing $\alpha \sim y^4$ does very well here, as does writing $\alpha \sim x^2$. To confirm these results, we show the same plots with α determined so as to modify the correlation hole from s -functions alone, in Figures 7–11 and 7–12. Now, α fits rather more poorly to the powers of x and y chosen, although the general trend is still clear.

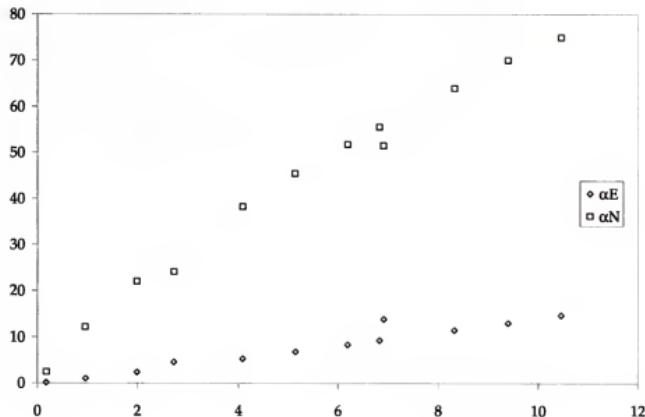


Figure 7–11: Cutoff parameter α from the s basis set vs. the gradient parameter x^2

The slope of the α_N line depends on whether we are modifying the s - or sp -correlation hole, and similarly for the α_E ; these lines appear to be coalescing as we go to higher angular momenta included in the basis set, although this conclusion is certainly tentative.

Nevertheless, it appears that we may be able to write α as a functional of the density and, perhaps, its gradient, and that the functional used will depend on properties of the basis set. This is encouraging indeed, as if we can successfully write α as such a functional, we may evaluate it from a simple density and use it in a more sophisticated correlated technique, which would enable us to perform

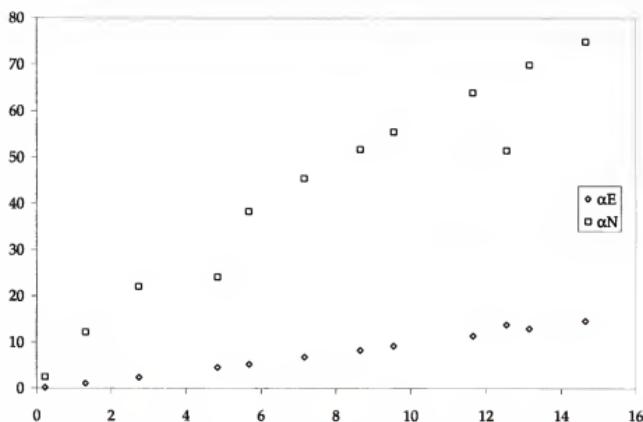


Figure 7-12: Cutoff parameter α from the s basis set vs. the screening parameter y^4

basis set corrected calculations in a fraction of the time it would take for similarly accurate calculations in a larger basis set.

That α fits so well on these lines may be a simple artifact; we have a rather limited selection of systems from which to get data points, and this initial determination is in need of much investigation. We feel that these preliminary results are encouraging and provide them as a prospect for future development.

Having extracted all that we can from the approximation that the cutoff function is $f(u) = e^{-\alpha u^2}$, with α determined from the system average of some density dependent quantities, we now wish to relax this rather severe approximation. It seems more reasonable, after all, that the cutoff length depend on the location of the electron pair's center of mass, and that we should write instead $f(\mathbf{R}, u) = e^{-\alpha(\mathbf{R})u^2}$ and take the system average of this more complicated quantity.

Physically, this can be seen in the following light. If we write the correction to the spherically averaged but not system averaged correlation hole as

$$\delta\langle n_c(\mathbf{R}, u) \rangle = f(\mathbf{R}, u) \langle n_c^{LDA}(\mathbf{R}, u) - n_c^{WFT}(\mathbf{R}, u) \rangle, \quad (7.7)$$

and system average the entire quantity, we would have a rather complicated system average to perform. However, if we denote the system average of some quantity g by \bar{g} and the deviations from that average by \tilde{g} , we could write the system average of our correction as

$$\delta\bar{n}_c(u) = \bar{f}(u)(\bar{n}_c^{LDA}(u) - \bar{n}_c^{WFT}(u)) + \overline{\tilde{f}(\mathbf{r}, u)(\tilde{n}_c^{LDA}(\mathbf{R}, u) - \tilde{n}_c^{WFT}(\mathbf{R}, u))}, \quad (7.8)$$

where we have used the fact that the system average of \tilde{g} is \bar{g} , and the system average of \tilde{g} is zero.

Thus, writing

$$\delta\bar{n}_c(u) = \bar{f}(u) (\bar{n}_c^{LDA}(u) - \bar{n}_c^{WFT}(u)), \quad (7.9)$$

as we wish to do, can be seen as an approximation wherein we first correct the spherically averaged but not system averaged correlation hole, then system average the result, neglecting the average of the product of fluctuations. It would be useful indeed if we had some fruitful scheme to approximate this neglected term, but no such scheme is apparent.

It yet remains to evaluate the system average of $f(\mathbf{R}, u)$. We could, if we so desired, construct this directly, but we would prefer to avoid the need to do so, since we would need to perform a system average for each value of u , thus making the cutoff function something we would have to tabulate, and no longer a simple analytic function. This would make the resulting energy integrals rather cumbersome, and we thus prefer to have an analytic form for $\bar{f}(u)$.

To this end, we write

$$\alpha(\mathbf{R}, u) = C k_S^4(\mathbf{R}, u) = \bar{\alpha}(1 + \delta(\mathbf{R})), \quad (7.10)$$

where $\bar{\alpha}$ is the system average of α , and therefore

$$\int d\mathbf{R} n(\mathbf{R}) \delta(\mathbf{R}) = 0. \quad (7.11)$$

Writing, for the sake of brevity,

$$y_q = \int d\mathbf{R} \frac{n(\mathbf{R})}{N} k_S^q(\mathbf{R}), \quad (7.12)$$

we also have

$$\bar{\alpha} = Cy_4. \quad (7.13)$$

Note that we have here neglected gradient contributions; the idea is that the effects of gradients would be brought in by letting α be a function of \mathbf{R} rather than just a constant.

With these conventions, the system average of $f(\mathbf{R}, u)$ is

$$\bar{f}(u) = \int d\mathbf{R} \frac{n(\mathbf{R})}{N} e^{-\bar{\alpha}(1+\delta(\mathbf{R}))u^2} \quad (7.14a)$$

$$= e^{-\bar{\alpha}u^2} \int d\mathbf{R} \frac{n(\mathbf{R})}{N} e^{-\bar{\alpha}\delta(\mathbf{R})u^2} \quad (7.14b)$$

$$= e^{-\bar{\alpha}u^2} \sum_{p=0}^{\infty} \frac{(-\bar{\alpha}u^2)^p}{p!} \int d\mathbf{R} \frac{n(\mathbf{R})}{N} \delta^p(\mathbf{R}). \quad (7.14c)$$

Using the binomial theorem, with

$$\delta(\mathbf{R}) = \frac{k_S^4(\mathbf{R})}{y_4} - 1, \quad (7.15)$$

we obtain

$$\bar{f}(u) = e^{-\bar{\alpha}u^2} \sum_{p=0}^{\infty} \frac{(-\bar{\alpha}u^2)^p}{p!} \sum_{q=0}^p \binom{p}{q} \int d\mathbf{R} \frac{n(\mathbf{R})}{N} \left(-\frac{k_s^4(\mathbf{R})}{y_4} \right)^q \quad (7.16a)$$

$$= e^{-\bar{\alpha}u^2} \sum_{p=0}^{\infty} \frac{(-\bar{\alpha}u^2)^p}{p!} \sum_{q=0}^p \binom{p}{q} \frac{y_{4q}}{(-y_4)^q}. \quad (7.16b)$$

We will use this final expression, (7.16b) as a more sophisticated model for the cutoff function, truncating the sum over p at some small value.

There are a few things which should be pointed out about the summation. First, in the HEG limit, where $\delta = 0$, we have simply $\bar{f}(u) = e^{-\bar{\alpha}u^2}$. Thus, our approximation will certainly be exact for an HEG. Second, the $p = 0$ term of the sum is just 1, so that if we retain only that much, this version of the cutoff function is similar to what we have used previously, again yielding the HEG result. Finally, the $p = 1$ term vanishes; this is most easily seen from (7.14c), wherein it becomes clear that the $p = 1$ term corresponds to the system average of δ , which vanishes by construction. Corrections, then, to the HEG limit are of order u^4 .

7.6 A Final Assessment for Two-Electron Systems

We now have many possibilities to sort through with regards to the model. First, we have the option of including gradient corrections to the LDA hole or not including them. Secondly, we have the option of truncating the sum of (7.16b) after $p = 0$ or including terms with $p = 2$ or higher. In none of these cases will the basic results change significantly, as far as total energy from the model is concerned, since the broad general features are already in place with the LDA hole and the simple cutoff function, and any refinements we might make occur at larger values of u . What will change is the results for the parameter C of (7.13).

We summarize those results in Table 7-4, wherein we show the value of C required to satisfy the sum rule to the desired 0.001 with and without the addition of the gradient corrections to the hole (as indicated by the presence or absence of

the subscript g), and with the sum over p truncated at $p = 0$ and at $p = 2$ (as indicated by the superscript). We have not included the energies, as truncating the sum over p at $p = 0$ or $p = 2$ changes the energy by no more than $0.1 mE_H$ in any of these systems. Also, because our model breaks down at least partially for hydride and Hooke's atom at $\omega = \frac{1}{10}$, we have omitted these two systems from consideration at present.

Table 7-4: Constants in the assorted test systems

System	C^0	C_g^0	C^2	C_g^2
$Z = 2$	1.006	0.570	1.895	1.110
$Z = 3$	1.035	0.716	1.900	1.330
$\omega = 0.5$	1.520	1.020	2.040	1.360
$\omega = 1$	1.600	1.230	2.140	1.640
$\omega = 2$	1.540	1.260	2.070	1.690
$\omega = 2.5$	1.500	1.240	2.020	1.660
$\omega = 3$	1.460	1.220	1.970	1.630
$\omega = 3.3$	1.440	1.210	1.950	1.620
$\omega = 4$	1.400	1.175	1.890	1.580
$\omega = 4.5$	1.370	1.155	1.850	1.550
$\omega = 5$	1.345	1.135	1.820	1.520
Mean	1.383	1.085	1.959	1.517
Deviation	0.195	0.230	0.100	0.179
% Deviation	14%	21%	5%	12%

Clearly, C is not constant as we might wish it to be. These results are somewhat misleading, however; in Figure 7-10, the line of α vs. y_1^4 appears to fit all the points reasonably well, and the variation in the ratio $\frac{\alpha}{y_1^4}$ is comparable to the variation in C across the test systems. Also clearly, the deviation in C decreases as we increase the number of terms retained in the summation, as one would hope if the scheme is to be sensible.

With this in mind, we show one final table, Table 7-5. In this table, we present the results in which we have neglected gradient corrections, truncated the summation of (7.14c) at $p = 2$, and used $C = 1.959$, the average value across our test systems. The last column is the amount by which the sum rule for the

correlation hole is violated; in other words, it is

$$\delta N = \int_0^\infty du 4\pi u^2 \delta \bar{n}_c(u). \quad (7.17)$$

The energies are errors relative to the complete basis limit.

Table 7–5: Errors in the assorted test systems

System	$\bar{\alpha}$	ΔE_{sp}	ΔE_{spd}	$\Delta \bar{E}_{sp}$	δN
$Z = 2$	13.6	0.0039	0.0013	0.0023	-0.0009
$Z = 3$	34.6	0.0039	0.0012	0.0005	-0.0009
$\omega = 0.1$	0.494	0.0005	0.0001	0.0002	-0.0005
$\omega = 0.5$	2.96	0.0026	0.0007	0.0007	-0.0011
$\omega = 1$	6.23	0.0037	0.0011	0.0007	-0.0012
$\omega = 2$	12.9	0.0047	0.0014	0.0005	-0.0011
$\omega = 2.5$	16.3	0.0050	0.0016	0.0005	-0.0011
$\omega = 3$	19.8	0.0052	0.0016	0.0005	-0.0010
$\omega = 3.3$	21.8	0.0053	0.0016	0.0004	-0.0010
$\omega = 4$	26.6	0.0056	0.0017	0.0004	-0.0009
$\omega = 4.5$	30.1	0.0057	0.0018	0.0004	-0.0009
$\omega = 5$	33.5	0.0057	0.0018	0.0003	-0.0009
Mean Error		0.0043	0.0013	0.0006	-0.0010

With this table, we begin to see the utility of the scheme. Although we have not actually chosen the constant C to satisfy the sum rule to the desired tolerance, we in fact do satisfy the sum rule to within, or nearly within, the desired tolerance in all our systems. This enables us to pick a value for C ahead of time, and obviates the need to even construct the correlation hole. So long as we can obtain a reasonable approximation to the density (by means, for example, of a normal DFT calculation), we can construct a cutoff function which should yield a correlation hole that satisfies the sum rule to good accuracy, and we can then carry out standard wavefunction calculations with the small *sp*-complete basis set and use the correction to obtain accuracy which is comparable to or better than that in the more expensive *spd*-complete basis set.

Evaluating the energy correction requires only constructing Ξ and calculating the integrals of $f(u)/u$, as well as evaluating the LDA contribution numerically, all as sketched in Chapter 5. Thus, the proposed model is no more expensive than a standard wavefunction calculation in a polarized basis but affords accuracy comparable to that of a standard wavefunction calculation in a much more extensive basis, at least in the systems examined to date.

7.7 Results for Neon

Lest it be thought that only for small systems does the proposed model work reasonably well, we examine the neon atom as well. Admittedly, this is also not a vast system, but we wish only to show that the good results are not mere artifacts of two-electron systems. Larger systems yet could certainly be handled by the model, since the only truly time-consuming part is building the correlation hole and in real applications the correlation hole need not be obtained.

In the case of the neon atom, the Full CI two-matrix and one-matrix are beyond our ability to obtain, so we must make do with a wavefunction which has not only error due to the finite basis set but also error due to incomplete electron correlation. We use density-matrices complete through third order in perturbation theory in this portion of the work.

To obtain a basis, we use the exponents of the AUG-CC-PV5Z of Dunning and coworkers [88] and decontract the basis. These yield the energies listed in Table 7–6 as ‘*sp*’ and ‘*spd*,’ in which we used only the exponents for *s*- and *p*-functions and for *s*-, *p*-, and *d*-functions, respectively. Unfortunately, the calculation also using *f*-functions does not converge when the basis is decontracted, so that for this result, we have used the contracted form of the basis. Since the error made in using the contracted *spd*-basis is some $20mE_H$, we expect that the error using the contracted *spdf*-basis is of the same order, so that the results are rather superior to

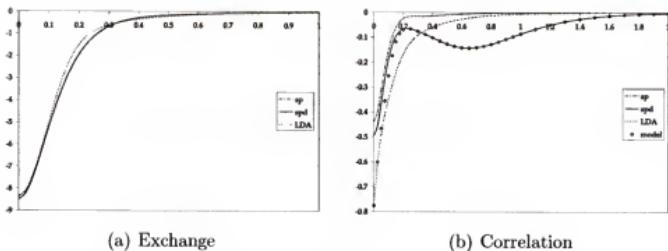


Figure 7-13: Exchange and Correlation Holes in Neon.

those from our model (listed as 'model' in the table, and with the correlation hole built using the *spd*-basis result).

Table 7-6: Total energies in the neon atom

Basis	Energy (E_H)	Error (- mE_H)
<i>sp</i>	-128.73395	200.7
<i>spd</i>	-128.86145	73.2
<i>spdf</i>	-128.88437	50.2
Complete (est.)	-128.9346	0.0
model	-128.87219	62.4

Nevertheless, even with this rather crude description of the density matrices, our model offers a fair amount of improvement over the initial description. Further, since the basis set is unfortunately not saturated with respect to *d*-functions, we expect we should actually obtain somewhat more improvement than we see here. It is clear that as we move to larger systems, the effects of using our model are less dramatic, but they are certainly non-negligible. The exchange and correlation holes obtained are plotted in Figures 7-13a and 7-13b, respectively. Note the shell structure in the correlation hole. In passing, we note that the value of the parameter C^0 in writing $\alpha = C^0 y_4$ is 1.344, in excellent agreement with what we observe for smaller systems; this seems to render our contention that we should write the cutoff length in this manner incontrovertible.

CHAPTER 8 CONCLUSIONS

While the theory of electron correlation is formally understood *in toto*, the resulting equations cannot be solved except in a finite basis set. Unfortunately, the convergence of correlated energies (and by extension, of most properties of interest) with respect to basis set size is extremely slow, and to date no affordable way of estimating the complete basis set limit has been found. The practicing quantum chemist must follow one of three paths to reach the goal of basis set converged results.

One alternative is to extrapolate to estimate the basis set limit, but because this procedure requires multiple calculations it is somewhat unwieldy, and more importantly, the process complicates the construction of analytical energy derivatives, without which only a few problems of chemical interest can be solved. A second alternative is to use one of a variety of sophisticated approaches towards reducing the basis set error, such as the explicitly correlated R12 methods of Kutzeligg and coworkers or the transcorrelated Hamiltonian approach of Boys and Handy. These schemes, while exact, systematic, and differentiable, require the evaluation of complicated many-body integrals, and are thus rather expensive themselves. The final alternative to date is to use one of the rather unsystematic approximate potential approaches. These approaches are computationally affordable and differentiable, but can never yield the exact result except by coincidence. It is our belief that this state of affairs constitutes the largest unresolved difficulty in the application of correlated wavefunction techniques to problems of chemical interest.

In this work, we have proposed an alternative which combines most of the best features of these approaches. Our alternative is conceptually straightforward,

analytic and hence differentiable, accurate under ordinary circumstances, and yet is little more expensive than the standard *ab initio* calculation on which it is based.

The fundamental reason that correlated results converge only slowly with respect to the size of the basis is that the short-range electronic interaction is poorly approximated in a one-particle basis, and requires high angular momentum functions for an accurate description. Approximating the effects of high angular momentum functions (and hence approximating the angular correlation) is our route towards near basis set limit results. This is done through the analytic local density approximation for the short-range correlation hole. By switching smoothly from a local density description to a conventional *ab initio* description, we may model the correlation hole in a way which is more accurate than either the wavefunction approach or the local density approach separately.

Choosing the switching function to conserve particle number and approximating the effects of density variations in the system allows us to provide a model which has one adjustable parameter which is determined in principle by the basis set and level of correlation. Making this determination yields results for total energies which are comparable to or superior than results in large bases while requiring only fairly small bases for the actual calculation. Only in situations in which the correlation has a substantial radial contribution does the model fail to provide significant improvement at an insignificant cost.

Our approach is not, of course, without room for improvement. Principally, we have not carried out the fully self-consistent calculations. Doing so would have many benefits: N-representability and proper normalization would be ensured, and all properties and excited states would be corrected for short-range correlation. At the same time, the optimal value for the parameter C might change. Too, we would like a more accurate model yet for the short-range correlations, and in particular one which might overcome the problems associated with strong radial correlation.

Finally, we have neglected the last term of (7.8), and putting these terms back into the theory in some reasonable manner would be very much of interest.

We offer this approach to the quantum chemistry community with the expectation that many improvements can be made to the basic idea, and with hope that it will find considerable success in making reliable correlated calculations much more routinely applicable than they have been to date, thereby finally allowing practicing quantum chemists to get the right results for the right reasons and in the right systems.

APPENDIX A SECOND QUANTIZATION AND DIAGRAMMATIC TECHNIQUES

In moving beyond Hartree-Fock theory and into correlated methods, one is soon faced with algebra which is complicated enough that it warrants using special methods to solve the equations. The format with which we work is diagrammatic perturbation theory (and, of course, its extension to coupled-cluster theory), which allows us to represent terms in our equations pictorially. The complicated algebra which we must do is thereby reduced to drawing all the needed diagrams and then interpreting them as terms in an equation. This greatly facilitates correlated techniques. We shall discuss diagrammatics presently, but it will be useful to give a brief review of second quantization before we do so.

A.1 Second Quantization

The basic idea of second quantization is that it is more convenient to work explicitly in a basis from the beginning. To this end, we define an electronic state as a collection of individual determinants built by adding electrons to particular orbitals and weighted by coefficients which we can choose freely. For simplicity, we shall here take our basis to consist of orthonormal spinorbitals, but this is not necessary.

A.1.1 Electron Field Operators

We begin by defining a state with no electrons at all, the physical vacuum. This state, represented here by $|\Omega\rangle$, is assumed to have unit normalization. We then build all possible one-electron states by adding a single electron in all possible ways, and similarly for states with larger numbers of electrons. This is accomplished through the use of creation operators, written here as c_p , which are defined through their action on some electronic state (NB: our notation for the creation

operators is exactly opposite that which most authors use). If we write some single determinant as $|\varphi_p\varphi_q\varphi_r\dots\rangle$, where it is to be understood that orbitals p, q, r , and so forth are occupied, then we have

$$c_x |\varphi_p\varphi_q\varphi_r\dots\rangle = |\varphi_x\varphi_p\varphi_q\varphi_r\dots\rangle, \quad (\text{A.1})$$

a single determinant with one more electron.

With the capability of adding electrons to states, we must also have the ability to remove them. We do this through annihilation operators, written as c^p ; as the notation suggests, the creation operators are the adjoints of the annihilation operators. We require that attempting to remove an electron from an orbital which has no electrons in it gives zero. The set of all creation operators and all annihilation operators form the field operators.

Because determinantal wavefunctions are antisymmetric, we need to worry a little about phase conventions. We simply assume that creation operators put electrons in the first position in the determinant, while annihilation operators remove them from the first orbital in the determinant. If the determinant is not written in the proper order, we can simply reorder it at the cost of a sign. Thus, we have

$$c^p |\varphi_p\varphi_q\varphi_r\dots\rangle = |\varphi_q\varphi_r\dots\rangle, \quad (\text{A.2})$$

but

$$c^p |\varphi_q\varphi_p\varphi_r\dots\rangle = -|\varphi_q\varphi_r\dots\rangle. \quad (\text{A.3})$$

In neither of the above two equations is a summation over p to be taken.

In fact, the above phase convention is a consequence of canonical anticommutation. Since electrons are fermions and we must have antisymmetry built into our wavefunction, we know that the electron creation operators must anticommute. This can be easily seen by comparing the determinants $|\varphi_p\varphi_q\rangle$ and

$|\varphi_q \varphi_p\rangle = -|\varphi_p \varphi_q\rangle$. Obviously, the first determinant is constructed by

$$|\varphi_p \varphi_q\rangle = c_p c_q |\Omega\rangle, \quad (\text{A.4})$$

while the second is constructed by

$$|\varphi_q \varphi_p\rangle = c_q c_p |\Omega\rangle. \quad (\text{A.5})$$

For these two to be equal apart from the minus sign, we must require that

$$c_p c_q + c_q c_p = \{c_p, c_q\} = 0. \quad (\text{A.6})$$

Taking the adjoint of the anticommutator for creation operators immediately tells us that the annihilation operators anticommute as well. Lastly, for the mixed anticommutator with one creation operator and one annihilation operator, we have

$$\langle \varphi^p | \varphi_q \rangle = \langle \Omega | c^p c_q |\Omega\rangle = \delta_q^p. \quad (\text{A.7})$$

Because the annihilation operator annihilates the vacuum, we can write

$$c^p c_q |\Omega\rangle = [c_q c^p + \{c_q, c^p\}] |\Omega\rangle = \{c_q, c^p\} |\Omega\rangle. \quad (\text{A.8})$$

Thus, we see that

$$\langle \Omega | \{c^p, c_q\} | \Omega \rangle = \delta_q^p, \quad (\text{A.9})$$

and hence

$$\{c^p, c_q\} = \delta_q^p. \quad (\text{A.10})$$

A.1.2 The Fermi Vacuum and Particle-Hole Formalism

While the machinery we have just outlined is powerful, it is often somewhat inconvenient, and certainly can be less than transparent. It is typically better to work with respect to the Fermi vacuum than with respect to the true vacuum.

We write the Fermi vacuum in this work as $|0\rangle$ for the most part, though it is also written as $|\Phi\rangle$ or $|\Psi^{(0)}\rangle$ as well. The Fermi vacuum is simply some reference state

from which we wish to work, always taken to be a single determinant in this work, and usually (but not always) the Hartree-Fock determinant. We need not specify how many electrons are occupied in the Fermi vacuum, which is one of its great advantages.

A.1.3 Normal Ordering and Contractions

Particle-hole formalism is powerful, but evaluating expectation values of long strings of field operators is still often cumbersome. To simplify this, we introduce the concept of normal order. A string of field operators is said to be in normal order if all operators which annihilate the vacuum with respect to which we are normal ordering are to the right of all operators which do not annihilate that vacuum; we have, then, c^a and c_i to the right. This has the convenient property that the expectation value of a normal-ordered string of field operators with respect to the Fermi vacuum vanishes; either there is at least one annihilation operator, in which case it annihilates the vacuum, or there are none, in which case the expectation value of a string of creation operators is seen to be equivalent to the overlap between determinants with different numbers of electrons, which is identically zero as well. We indicate a string of operators to be in normal order by surrounding them with braces, so that the string $\{c_a c^b c_i c^j\}$ is understood to be in normal order, even though it is not explicitly written as such.

We must also introduce the concept of a contraction, which fundamentally is simply the result of anticommuting one field operator through another. The only non-zero contractions are between operators c_p and c^q ; the result of the contraction is $(-1)^\sigma \delta_p^q$, where σ is the number of field operators between c_p and c^q . Thus, for example, given the string $c_p c^q c_s c^r$, the contraction between c_p and c^q is simply δ_p^q , while with the string $c_p c_s c^q c^r$, the contraction between c_p and c^q is $-\delta_p^q$.

We can now take advantage of a powerful theorem known as Wick's theorem, the proof of which is beyond the scope of this appendix. Wick's theorem tells us

that in the time-independent case, a string of field operators can be written as the normal-ordered part, plus all terms in which there has been one contraction and the remaining operators are normal-ordered, plus all terms in which there have been two contractions and the remaining operators are normal-ordered, and so forth. Since the expectation value of any normal-ordered product vanishes when taken with respect to the Fermi vacuum, we know in particular that the expectation value of some string of field operators comes only from the fully contracted part. Thus, we see that we can immediately write

$$\langle 0 | c^a c^c c_b c_d | 0 \rangle = \delta_d^a \delta_b^c - \delta_b^a \delta_d^c, \quad (\text{A.11})$$

a result which we could have found by using anticommutation directly but which is simpler when done using Wick's theorem.

A.1.4 Second-Quantized Operators

The foregoing will have been useless unless we can use second quantization to evaluate expectation values of operators of interest. Fortunately, this is not particularly difficult, as we recall that any expectation value can be taken once we know the necessary density matrix. Thus, we need only evaluate the density matrices in second quantization and expectation values follow trivially. This is done in Appendix B for the general k -matrix; the result was quoted as (3.7). We also need the second-quantized form of the operator whose expectation value we are taking; this is given by

$$O = \frac{1}{k!} O_{p_1 \dots p_k}^{q_1 \dots q_k} c_{q_1} \dots c_{q_k} c^{p_1} \dots c^{p_k}. \quad (\text{A.12})$$

Expectation values then become

$$\langle O \rangle = O_{p_1 \dots p_k}^{q_1 \dots q_k} \Gamma_{q_1 \dots q_k}^{p_1 \dots p_k}. \quad (\text{A.13})$$

The most important second-quantized operator for our purposes is the Hamiltonian, written simply as

$$H = h_q^p c_p c^q + \frac{1}{4} g_{rs}^{[pq]} c_p c_q c^s c^r. \quad (\text{A.14})$$

The normal-ordered Hamiltonian is also of interest; it can be written as

$$H_N = H - \langle H \rangle, \quad (\text{A.15})$$

which becomes

$$H_N = F_q^p \{c_p c^q\} + \frac{1}{4} g_{rs}^{[pq]} \{c_p c_q c^s c^r\}, \quad (\text{A.16})$$

where F_q^p is a matrix element of the Fock operator. We thus see that the Fock operator appears naturally in working with the normal-ordered Hamiltonian, regardless of what source we choose for our orbitals.

A.2 Diagrammatics

While Wick's theorem allows us to evaluate matrix elements of field operators much more readily than by using simple anticommutation, the large strings of field operators involved in correlated techniques quickly become cumbersome even so. Thus, we turn to diagrammatic techniques. These allow us to derive some of the complicated equations we need quickly and easily.

The basic idea of diagrammatic techniques is to graphically represent the building blocks of second quantization, *i.e.* field operators and matrix elements. Field operators are represented by lines, and these lines meet at vertices, which represent matrix elements. Contractions are represented by two lines joining without a vertex. Thus, an arbitrary operator can be represented by an appropriate combination of vertices and lines. Once operators are represented, they can be combined as needed to form the whole diagram, and one can then use interpretation rules to find the algebraic analogue of the graph.

Working with the Fermi vacuum as we are, we have both upwards directed lines (corresponding to particles, or electrons in virtual orbitals) and downwards directed lines (corresponding to holes, or electrons in occupied orbitals). Lines entering a vertex correspond to annihilation operators, and lines leaving a vertex correspond to creation operators. Thus, from the direction and origin of a line, we can determine what kind of field operator it represents. Note that as the only non-vanishing contractions are between field operators of the same type (that is, between two particle operators or two hole operators), upwards lines must join with other upwards lines, and downwards lines must join with other downwards lines. Lines which connect two vertices are known as *internal* lines, while those which do not are *external* lines.

Since the external lines correspond to field operators, a diagram which has some number of external lines is an operator (such a diagram is called *open*), while a diagram which has none is a number and is called *closed*. Two pieces of a diagram are *connected* if there is at least one line joining them, while pieces which are not so joined are said to be *disconnected*. Diagrams are *linked* when none of the disconnected pieces are closed, while those diagrams which have closed disconnected pieces are *unlinked*. Because a closed piece of a diagram corresponds to just a number and disconnected pieces are separate terms which are to be multiplied together, unlinked diagrams correspond to the product of a number and either another number or an operator. In terms of algebraic formulae, connection of two terms is equivalent to summation over a common index.

The operator of primary interest to us is the Hamiltonian, the diagrammatic representation of which we present in Figure A-1 below.

$$\begin{aligned} H = & \quad \begin{array}{c} \text{---} \\ | \\ \times \end{array} + \begin{array}{c} \text{---} \\ | \\ \times \end{array} + \begin{array}{c} \diagup \\ \diagdown \\ \times \end{array} + \begin{array}{c} \diagup \\ \diagdown \end{array}^* \\ + & \begin{array}{c} \rangle \\ \cdots \\ \langle \end{array} + \begin{array}{c} \rangle \\ \cdots \\ \langle \end{array} + \begin{array}{c} \rangle \\ \cdots \\ \langle \end{array} \\ + & \begin{array}{c} \diagup \\ \diagdown \\ \text{---} \end{array} + \begin{array}{c} \diagup \\ \diagdown \\ \text{---} \end{array} + \begin{array}{c} \diagup \\ \diagdown \\ \text{---} \end{array} + \begin{array}{c} \diagup \\ \diagdown \\ \text{---} \end{array} \\ + & \begin{array}{c} \diagup \\ \diagdown \\ \text{---} \end{array} + \begin{array}{c} \diagup \\ \diagdown \\ \text{---} \end{array} \end{aligned}$$

Figure A-1: Hamiltonian diagrams

APPENDIX B DETAILS OF DENSITY MATRICES

Our goals in this appendix are two-fold. First, we wish to justify (3.7), our expression for the matrix elements of the k -particle density matrix elements. Second, we wish to provide a few details of the coupled-cluster one- and two-matrices. We begin with the former.

B.1 The k -Matrix as an Expectation Value

We write the (normalized) wavefunction in position space as

$$\Psi(\mathbf{X}_{1,N}) = M^{p_1 \dots p_N} \varphi_{p_1}(\mathbf{x}_1) \dots \varphi_{p_N}(\mathbf{x}_N), \quad (\text{B.1})$$

where M is antisymmetric on each pair of indices. The full N -matrix can thus be written as

$$n_N(\mathbf{X}_{1,N}; \mathbf{X}'_{1,N}) = M^{p_1 \dots p_N} M_{q_1 \dots q_N} \varphi_{p_1}(\mathbf{x}_1) \dots \varphi_{p_N}(\mathbf{x}_N) \varphi^{q_1}(\mathbf{x}'_1) \dots \varphi^{q_N}(\mathbf{x}'_N). \quad (\text{B.2})$$

The coefficients in the basis set representation are hence

$$\Gamma_{q_1 \dots q_N}^{p_1 \dots p_N} = M^{p_1 \dots p_N} M_{q_1 \dots q_N}. \quad (\text{B.3})$$

By repeated integrations, the basis set coefficients of the k -matrix are thus found to be

$$\Gamma_{q_1 \dots q_k}^{p_1 \dots p_k} = \binom{N}{k} M^{p_1 \dots p_k r_{k+1} \dots r_N} M_{q_1 \dots q_k r_{k+1} r_N}. \quad (\text{B.4})$$

Now, we would like to evaluate these coefficients as expectation values. First, however, we should note that in bra-ket notation, the wavefunction is

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} M^{p_1 \dots p_N} c_{p_1} \dots c_{p_N} |\Omega\rangle, \quad (\text{B.5})$$

where the factor of $\frac{1}{\sqrt{N!}}$ ensures proper normalization, as there are $N!$ equivalent orderings of the field operators in the above summations. It can readily be verified that the normalization implied by our initial position-space definition of the wavefunction is preserved by this form.

Bearing this in mind, consider the expectation value

$$G_{q_1 \dots q_k}^{p_1 \dots p_k} = \frac{1}{k!} \langle \Psi | c_{q_1} \dots c_{q_k} c^{p_k} \dots c^{p_1} | \Psi \rangle. \quad (\text{B.6})$$

Inserting the definition of the wavefunction, the right-hand side becomes

$$\frac{1}{k!N!} M_{s_1 \dots s_N} M^{r_1 \dots r_N} \langle \Omega | c^{s_N} \dots c^{s_1} c_{q_1} \dots c_{q_k} c^{p_k} \dots c^{p_1} c_{r_1} \dots c_{r_N} | \Omega \rangle. \quad (\text{B.7})$$

Now we anticomute the various c_q coefficients to the left. Since there are k different coefficients c_q and N different coefficients c_s , there will be $N!/(N - k)!$ terms which result from this anticommutation. However, each of these terms is identical; this is because they will each correspond to a different order of coefficients in M , and M is antisymmetric on interchange of any two of its indices. In other words, the antisymmetry in the string of operators $c^{s_N} \dots c^{s_1} c_{q_1} \dots c_{q_k}$ is compensated by the antisymmetry in the coefficient $M_{s_1 \dots s_N}$. The result is that we can use this antisymmetry to write only one of the terms, multiplying the entire thing by the number of terms. We thus get, by moving the coefficients c_q to the left,

$$\frac{1}{k!N!} \frac{N!}{(N - k)!} M_{q_1 \dots q_k s_{k+1} \dots s_N} M^{r_1 \dots r_N} \langle \Omega | c^{s_N} \dots c^{s_{k+1}} c^{p_k} \dots c^{p_1} c_{r_1} \dots c_{r_N} | \Omega \rangle. \quad (\text{B.8})$$

In precisely the same manner, we can anticomute the various c^p coefficients to the right, getting an identical multiplicative factor and leaving us with

$$\frac{1}{k!N!} \left(\frac{N!}{(N - k)!} \right)^2 M_{q_1 \dots q_k s_{k+1} \dots s_N} M^{p_1 \dots p_k r_{k+1} \dots r_N} \langle \Omega | c^{s_N} \dots c^{s_{k+1}} c_{r_{k+1}} \dots c_{r_N} | \Omega \rangle. \quad (\text{B.9})$$

We can now anticomute the remaining coefficients; once again, we use antisymmetry to combine the terms, which are $(N - k)!$ in number. Our final result is hence simply

$$G_{q_1 \dots q_k}^{p_1 \dots p_k} = \frac{(N - k)!}{k! N!} \left(\frac{N!}{(N - k)!} \right)^2 M_{q_1 \dots q_k r_{k+1} \dots r_N} M^{p_1 \dots p_k r_{k+1} \dots r_N}, \quad (\text{B.10})$$

or, cancelling the appropriate combinatoric factors,

$$G_{q_1 \dots q_k}^{p_1 \dots p_k} = \binom{N}{k} M_{q_1 \dots q_k r_{k+1} \dots r_N} M^{p_1 \dots p_k r_{k+1} \dots r_N}. \quad (\text{B.11})$$

This is the result we sought, verifying that the coefficients of the k -matrix are given by

$$\Gamma_{q_1 \dots q_k}^{p_1 \dots p_k} = \frac{1}{k!} \langle \Psi | c_{q_1} \dots c_{q_k} c^{p_k} \dots c^{p_1} | \Psi \rangle. \quad (\text{B.12})$$

B.2 Expressions for the Coupled-Cluster Density Matrices

Deriving the expressions for the CCSD one-matrix and two-matrix is often tedious but never particularly difficult or instructive. Hence, we merely quote the results and outline a general strategy by which one may obtain them.

To begin with, then, it is all but essential to take proper advantage of antisymmetry, as we did earlier in this appendix. It proves convenient to group terms according to those which have similar types of T and Λ operators, which helps in showing the cancellation of unlinked diagrams. Lastly, anticommutation of field operators produces strings of Kronecker deltas, and it proves convenient to manipulate these strings as much as possible before carrying out the summations.

The results for the normal-ordered part of the one matrix are

$$\bar{\gamma}_i^j = -\lambda_a^j t_i^a - \frac{1}{2} \lambda_{ab}^{jk} t_{ik}^{ab}, \quad (\text{B.13a})$$

$$\bar{\gamma}_i^a = t_i^a + 4\lambda_b^j t_i^b t_j^a + \frac{1}{2} \lambda_{cd}^{kl} (t_l^a t_{ik}^{cd} + t_i^c t_{kl}^{da}), \quad (\text{B.13b})$$

$$\bar{\gamma}_a^i = \lambda_a^i, \quad (\text{B.13c})$$

$$\bar{\gamma}_a^b = \lambda_a^j t_j^b + \frac{1}{2} \lambda_{ac}^{jk} t_{jk}^{bc}. \quad (\text{B.13d})$$

The reader may readily verify that $\text{tr}(\bar{\gamma}) = 0$.

The true two-particle part of the two-matrix is more complicated. To simplify the equations somewhat, we define

$$\tau_{ij}^{ab} = t_{ij}^{ab} + 2t_i^a t_j^b. \quad (\text{B.14})$$

Also, recall that enclosing two indices in brackets indicates explicit antisymmetrization on those two indices, so that, for example,

$$\tau_{[ij]}^{ab} = \tau_{ij}^{ab} - \tau_{ji}^{ab}. \quad (\text{B.15})$$

With these simplifying definitions, we may write the two-particle part of the two-matrix as

$$\bar{\Gamma}_{ab}^{kl} = \frac{1}{2}\lambda_{ab}^{kl}, \quad (\text{B.16a})$$

$$\bar{\Gamma}_{ib}^{kl} = -\frac{1}{2}\lambda_{ab}^{kl}t_i^a, \quad (\text{B.16b})$$

$$\bar{\Gamma}_{ij}^{kl} = \frac{1}{4}\lambda_{ab}^{kl}\tau_{ij}^{ab}, \quad (\text{B.16c})$$

$$\bar{\Gamma}_{ab}^{kd} = \frac{1}{2}\lambda_{ab}^{kl}t_l^d, \quad (\text{B.16d})$$

$$\bar{\Gamma}_{ib}^{kd} = -\frac{1}{2}\lambda_b^k t_i^d - \frac{1}{4}\lambda_{ab}^{kl}(t_{il}^{ad} + \tau_{il}^{ad}), \quad (\text{B.16e})$$

$$\bar{\Gamma}_{ij}^{kd} = -\frac{1}{4}\lambda_c^k \tau_{[ij]}^{cd} + \frac{1}{4}\lambda_{ab}^{kl}(t_l^d \tau_{ij}^{ab} + 3t_{l[i}^a t_{j]}^d), \quad (\text{B.16f})$$

$$\bar{\Gamma}_{ab}^{cd} = \frac{1}{4}\lambda_{ab}^{ij}\tau_{ij}^{cd}, \quad (\text{B.16g})$$

$$\bar{\Gamma}_{ib}^{cd} = \frac{1}{4}\lambda_b^k \tau_{[ik]}^{cd} - \frac{1}{4}\lambda_{ab}^{kl}(t_i^a \tau_{kl}^{cd} + 3t_{ik}^a t_l^d), \quad (\text{B.16h})$$

$$\begin{aligned} \bar{\Gamma}_{ij}^{cd} &= \frac{1}{4}\tau_{[ij]}^{cd} + \frac{1}{4}\lambda_e^m \left(\tau_{[ij]}^{e[c} t_m^{d]} + 6t_{m[i}^e t_{j]}^d \right) + \frac{1}{8}\lambda_{ef}^{mn} \tau_{ij}^{ef} \tau_{mn}^{cd} \\ &+ \frac{1}{4}\lambda_{ef}^{mn} \left(t_{mn}^{e[c} t_{[i}^{d]} f] + t_{m[i}^e t_{j]}^{[c} t_m^{d]} + 8t_n^e t_{mi}^{de} t_j^f \right) \\ &+ \frac{1}{4}\lambda_{ef}^{mn} \left(t_{m[i}^{cd} t_{j]}^{ef} + t_{mn}^{e[c} t_{ij}^{d]} + 2t_{mi}^{e[c} t_{jn}^{d]} \right). \end{aligned} \quad (\text{B.16i})$$

Again, with some exertion, the appropriate sum rules are seen to be satisfied.

APPENDIX C SPECIAL FUNCTIONS

Several special functions appear throughout the text. For convenience, we present a few details here, although a more thorough discussion of the various functions is somewhat beyond the scope of this work.

C.1 Hermite Polynomials

The Hermite polynomials are a set of polynomials which solve the Hermite differential equation

$$\frac{d^2y(x)}{dx^2} - 2x \frac{dy(x)}{dx} + 2ny(x) \quad (\text{C.1})$$

for n a non-negative integer. An explicit solution can be constructed, as

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}, \quad (\text{C.2})$$

so that the first few Hermite polynomials are

$$H_0(x) = 1 \quad (\text{C.3a})$$

$$H_1(x) = 2x \quad (\text{C.3b})$$

$$H_2(x) = 4x^2 - 2 \quad (\text{C.3c})$$

$$H_3(x) = 8x^3 - 12x. \quad (\text{C.3d})$$

The polynomials of even order are even, and those of odd order are odd. They obey the orthogonality condition

$$\int_{-\infty}^{\infty} dx H_n(x) H_m(x) = 2^n n! \sqrt{\pi} \delta_{mn}. \quad (\text{C.4})$$

Of particular relevance for our purposes is the value of the Hermite polynomials at the origin, which is

$$H_{2n}(0) = (-2)^n(2n-1)!! \quad (\text{C.5a})$$

$$H_{2n+1}(0) = 0. \quad (\text{C.5b})$$

C.2 The Error Function

The error function appears quite regularly in Hooke's atom, both in the density and in the Coulomb hole. We will not discuss it at length, but a few details may be useful in extracting the limiting behavior of the density and the Coulomb hole.

The error function is the (normalized) integral of a Gaussian over a finite range,

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x dt e^{-t^2}. \quad (\text{C.6})$$

Clearly, the function is odd, so that

$$\text{erf}(-x) = -\text{erf}(x). \quad (\text{C.7})$$

The first derivative is

$$\frac{d}{dx} \text{erf}(x) = \frac{2}{\sqrt{\pi}} e^{-x^2}, \quad (\text{C.8})$$

and by (C.2), it can be seen that in fact

$$\frac{d^n}{dx^n} \text{erf}(x) = (-1)^{n-1} \frac{2}{\sqrt{\pi}} H_{n-1}(x) e^{-x^2}. \quad (\text{C.9})$$

One can obtain the series expansion of the error function by expanding the exponential in (C.6) in Taylor series and integrating; the result is

$$\text{erf}(x) = \frac{2x}{\sqrt{\pi}} \left(1 - \frac{1}{3}x^2 + \frac{1}{10}x^4 + \mathcal{O}(x^6) \right), \quad (\text{C.10})$$

so that in particular the frequently appearing ratio $\text{erf}(ax)/x$ becomes

$$\frac{\text{erf}(ax)}{x} = \frac{2a}{\sqrt{\pi}} \quad (\text{C.11})$$

in the limit as x goes to zero. The asymptotic expansion of the error function is

$$\text{erf}(x) = 1 - e^{-x^2} \frac{1}{\sqrt{\pi}} \left(\frac{1}{x} - \frac{1}{2x^3} + \mathcal{O}\left(\frac{1}{x^5}\right) \right). \quad (\text{C.12})$$

C.3 Spherical Bessel Functions

Spherical Bessel functions ultimately arise from writing the Helmholtz equation in spherical coordinates and searching for a product form of the solution. Brief manipulation brings one to the spherical Bessel differential equation,

$$t^2 \frac{d^2}{dt^2} f(t) + 2t \frac{d}{dt} f(t) + (t^2 - n(n+1)) f(t) = 0. \quad (\text{C.13})$$

This can be transformed into the Bessel differential equation by writing

$$f(t) = \frac{F(t)}{\sqrt{t}}. \quad (\text{C.14})$$

with the result that we can define two forms of spherical Bessel functions,

$$j_n(t) = \sqrt{\frac{\pi}{2t}} J_{n+\frac{1}{2}}(t) \quad (\text{C.15})$$

$$n_n(t) = \sqrt{\frac{\pi}{2t}} Y_{n+\frac{1}{2}}(t) \quad (\text{C.16})$$

where J and Y are the standard Bessel functions.

There are several useful recursion relations for the spherical Bessel functions. Of these, the most important for our purposes are the upwards recursion relation

$$f_{n+1}(t) = \left[\frac{n}{t} - \frac{d}{dt} \right] f_n(t) \quad (\text{C.17})$$

and the downward recursion relations

$$f_{n-1}(t) = \left[\frac{n+1}{t} + \frac{d}{dt} \right] f_n(t). \quad (\text{C.18})$$

By multiplying the downward recursion relation (C.18) by $f_n(t)$, using the upward recursion relation, and rearranging, we arrive at

$$\frac{f_n(t)^2}{t} = \frac{n-1}{n+1} \frac{f_{n-1}(t)^2}{t} - \frac{1}{2(n+1)} \frac{d}{dt} (f_n(t)^2 + f_{n-1}(t)^2). \quad (\text{C.19})$$

Spherical Bessel functions of the first kind (*i.e.*, the functions j_n) are what will chiefly concern us here, due to their regularity at the origin. For small t , they can be expanded as

$$j_n(t) = \frac{t^n}{(2n+1)!!} \left[1 - \frac{\frac{1}{2}t^2}{1!(2n+3)} + \frac{\left(\frac{1}{2}t^2\right)^2}{2!(2n+3)(2n+5)} - \dots \right], \quad (\text{C.20})$$

so that the $t = 0$ limit of the HEG one-matrix is

$$n(\mathbf{R}) = \lim_{t \rightarrow 0} \frac{k_F^3 j_1(t)}{\pi^2 t} = \frac{k_F^3}{3\pi^2}. \quad (\text{C.21})$$

This, in turn, means that the $t = 0$ limit of the kinetic energy density is given by

$$\tau(\mathbf{R}) = -\frac{1}{8} \nabla_R^2 n(\mathbf{R}) - \frac{1}{2} \lim_{t \rightarrow 0} 3n(\mathbf{R}) k_F(\mathbf{R})^2 \nabla_t^2 \frac{j_1(t)}{t} \quad (\text{C.22a})$$

$$= -\frac{1}{8} \nabla_R^2 n(\mathbf{R}) - \frac{1}{2} \lim_{t \rightarrow 0} \frac{3n(\mathbf{R}) k_F(\mathbf{R})^2}{t} \frac{d^2}{dt^2} j_1(t). \quad (\text{C.22b})$$

Using the series expansion for $j_1(t)$, we obtain

$$\tau(\mathbf{R}) = -\frac{1}{8} \nabla_R^2 n(\mathbf{R}) + \frac{3}{10} n(\mathbf{R}) k_F(\mathbf{r})^2. \quad (\text{C.23})$$

Finally, in the case of the exchange energy, we need to evaluate

$$I = \int_0^\infty dt \frac{j_1(t)^2}{t}. \quad (\text{C.24})$$

Inserting the recursion relation (C.19), we see that this is simply

$$I = -\frac{1}{4} \int_0^\infty dt \frac{d}{dt} [j_1(t)^2 + j_0(t)^2] = -\frac{1}{4} [j_1(t)^2 + j_0(t)^2] \Big|_0^\infty. \quad (\text{C.25})$$

We readily find that $j_1(\infty) = j_0(\infty) = j_1(0) = 0$, and that $j_0(0) = 1$, so that the entire integral becomes

$$I = -\frac{1}{4} \int_0^\infty dt \frac{d}{dt} [j_1(t)^2 + j_0(t)^2] = \frac{1}{4}. \quad (\text{C.26})$$

APPENDIX D HOOKE'S ATOM EXCHANGE-CORRELATION HOLE INTEGRALS

So as not to burden the disinterested reader with excessive time spent in evaluating the numerous integrals needed in constructing the Hooke's atom exchange-correlation hole, we have in several instances evaluated integrals without comment; the details are presented here.

The angular integrations all take one of two forms, either

$$\mathcal{I}_1 = \int d\Omega_u \int d\Omega_{r_1} e^{-\rho r_1^2 u} \quad (D.1)$$

or

$$\mathcal{I}_2 = \int d\Omega_u \int d\Omega_{r_1} r_{1u}^2 e^{-\rho r_1^2 u}. \quad (D.2)$$

Since the only angle present is that between r_1 and u , one of the solid angle integrals yields a simple 4π , and the azimuthal piece of the other solid angle integral gives another 2π . Thus, we have respectively

$$\begin{aligned} \mathcal{I}_1 &= 8\pi^2 \int_{-1}^1 dx e^{-\rho(r_1^2 + u^2 - 2ur_1x)} \\ &= 8\pi^2 e^{-\rho(r_1^2 + u^2)} \frac{\sinh(2\rho ur_1)}{\rho ur_1} \end{aligned} \quad (D.3)$$

and

$$\begin{aligned} \mathcal{I}_2 &= 8\pi^2 \int_{-1}^1 dx (r_1^2 + u^2 - 2ur_1x) e^{-\rho(r_1^2 + u^2 - 2ur_1x)} \\ &= 8\pi^2 e^{-\rho(r_1^2 + u^2)} (r_1^2 + u^2 \rho^{-1}) \frac{\sinh(2\rho ur_1)}{\rho ur_1} \\ &\quad - 16\pi^2 e^{-\rho(r_1^2 + u^2)} \frac{\cosh(2\rho ur_1)}{\rho}. \end{aligned} \quad (D.4)$$

Some radial integrals which appear frequently are

$$\mathcal{I}_3 = \int_0^\infty dr r^{2m} e^{-\rho r^2} \cosh(2\rho ur) \quad (\text{D.5})$$

and

$$\mathcal{I}_4 = \int_0^\infty dr r^{2m+1} e^{-\rho r^2} \sinh(2\rho ur). \quad (\text{D.6})$$

The second integral, conveniently, can be done in terms of the first, because

$$r \sinh(2\rho ur) = \frac{1}{2\rho} \frac{d}{du} \cosh(2\rho ur). \quad (\text{D.7})$$

Moreover, we can write

$$r^{2m} e^{-\rho r^2} = \lim_{\alpha \rightarrow 1} \left(-\frac{d}{d\alpha} \right)^m e^{-\alpha \rho r^2}, \quad (\text{D.8})$$

so that all we need is

$$\mathcal{I}_{3a} = \int_0^\infty dr e^{-\alpha \rho r^2} \cosh(2\rho ur). \quad (\text{D.9})$$

The integrand being even, we extend the range to run from $-\infty$ to ∞ and halve the result. We also convert the hyperbolic cosine into exponentials, so that we have

$$\mathcal{I}_{3a} = \frac{1}{4} \int_{-\infty}^\infty dr \left(e^{-\alpha \rho r^2 + 2\rho ur} + e^{-\alpha \rho r^2 - 2\rho ur} \right). \quad (\text{D.10})$$

Completing the square in each exponential gives us

$$\mathcal{I}_{3a} = \frac{1}{4} e^{\frac{\rho}{\alpha} u^2} \int_{-\infty}^\infty dr \left(e^{-\alpha \rho \left(r - \frac{u}{\alpha} \right)^2} + e^{-\alpha \rho \left(r + \frac{u}{\alpha} \right)^2} \right). \quad (\text{D.11})$$

At this point, the integral is trivial and we have, finally,

$$\mathcal{I}_{3a} = \frac{1}{2} \sqrt{\frac{\pi}{\alpha \rho}} e^{\frac{\rho}{\alpha} u^2}. \quad (\text{D.12})$$

Finally, for $\mathcal{I}_{1,3}$ and $\mathcal{I}_{2,3}$, we need integrals like

$$\mathcal{I}_4 = \int_{-\infty}^{\infty} dr \sin(kr) \sinh(ur) e^{-\alpha r^2} \quad (\text{D.13})$$

and its derivative with respect to u or α . Since this is the basic integral, we will evaluate only it. As we have done with \mathcal{I}_{3a} , we first convert the trigonometric functions into exponentials, obtaining

$$\mathcal{I}_4 = \frac{1}{4i} \int_{-\infty}^{\infty} dr e^{-\alpha r^2} (e^{v_+ r} + e^{-v_+ r} - e^{v_- r} - e^{-v_- r}), \quad (\text{D.14})$$

where we have defined $v_{\pm} = u \pm ik$. Completing the square in each term, we have

$$\begin{aligned} \mathcal{I}_4 &= \frac{1}{4i} e^{\frac{v_+^2}{4\alpha}} \int_{-\infty}^{\infty} dr \left(e^{-\alpha(r - \frac{v_+}{2\alpha})^2} + e^{-\alpha(r + \frac{v_+}{2\alpha})^2} \right) \\ &\quad - \frac{1}{4i} e^{\frac{v_-^2}{4\alpha}} \int_{-\infty}^{\infty} dr \left(e^{-\alpha(r - \frac{v_-}{2\alpha})^2} + e^{-\alpha(r + \frac{v_-}{2\alpha})^2} \right). \end{aligned} \quad (\text{D.15})$$

After carrying out the radial integral, and noting that $v_{\pm}^2 = u^2 - k^2 \pm 2iuk$, we have

$$\mathcal{I}_4 = \frac{1}{2i} \sqrt{\frac{\pi}{\alpha}} e^{\frac{u^2 - k^2}{4\alpha}} \left(e^{i\frac{uk}{2\alpha}} - e^{-i\frac{uk}{2\alpha}} \right). \quad (\text{D.16})$$

Finally, simplification yields

$$\mathcal{I}_4 = \sqrt{\frac{\pi}{\alpha}} \sin\left(\frac{uk}{2\alpha}\right) e^{\frac{u^2 - k^2}{4\alpha}}. \quad (\text{D.17})$$

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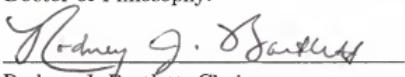
BIOGRAPHICAL SKETCH

Thomas M. Henderson was born in the state of Washington on November 16, 1976. He spent his formative years in various parochial schools before entering high school at Charles Wright Academy, where he was introduced to physics and chemistry for the first time and rapidly fell in love with the fields.

As an undergraduate, he studied at Harvey Mudd College (Claremont, California), completing an independent program of study that focused on both physics and chemistry. He worked under the guidance of Dr. Robert J. Cave, calculating matrix elements in electron-transfer reactions and eventually working on quasi-degenerate variational perturbation theory.

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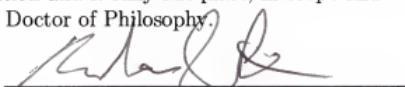
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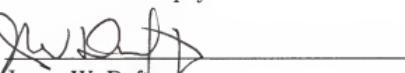
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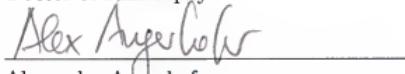
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May 2004

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